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54 Hair care compositions.

57 Hair care compositions which give both improved style retention and hair conditioning properties. The compositions comprise from about 0.01% to about 10% of a rigid silicone polymer and a volatile carrier.

Description

HAIR CARE COMPOSITIONS

TECHNICAL FIELD

5 The present invention relates to hair care compositions which have improved hair conditioning and style retention properties due to the inclusion of particular types of silicone polymers, and a volatile carrier for such polymers.

BACKGROUND OF THE INVENTION

10 The desire to have hair retain a particular shape is widely held. The two methodologies of accomplishing this are permanent chemical alteration of the hair or a temporary alteration. A temporary alteration is one which can be removed by water or by shampooing. This has generally been accomplished by means of the application of a separate composition to dampened hair, i.e., after shampooing and/or conditioning, and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have
15 been applied in the form of mousses, gels, lotions, and sprays. However, many people desire some improvement in style retention without the necessity of a separate step. Further, some people desire a high level of style retention such as that provided by a separate composition without the negative impact of these materials on dry hair properties, particularly ease of combing and hair feel.

20 Silicones in various hair care compositions have been disclosed in a large number of different publications, including U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader, issued December 21, 1981; U.S. Patent 4,341,799, Good, issued July 27, 1982; U.S. Patent 4,465,619, Boskamp, issued August 14, 1984; U.S. Patent 4,515,784, Bogartus, issued May 7, 1985; U.S. Patent 4,387,090, Bolich, issued June 7, 1983; and U.S. Patent 4,529,586, DeMarco et al, issued July 16, 1985.

25 It has now been discovered that hair care compositions comprising certain rigid silicone polymers and volatile carriers provide increased style retention. The compositions may be in any of the conventional forms, including but not limited to shampoos, conditioners, hairsprays, tonics, lotions and mousses. The compositions provide the increased style retention to the hair without decreasing dry hair properties such as ease of combing.

30 This is surprising since other silicone materials which have been typically used in hair care compositions as conditioners have hurt style retention, and the resins and gums used frequently for style retention have generally hurt dry hair properties such as combing.

It is an object of the present invention to provide hair care compositions which contain a high molecular weight rigid silicone polymer.

35 It is a further object of the present invention to provide stable hair care compositions containing a volatile carrier.

It is a further object of the present invention to provide hair care compositions providing good style retention.

It is a further object of the present invention to provide hair care compositions which provide good conditioning.

40 It is a further object of the present invention to provide an improved method of temporarily styling and conditioning hair.

It is a further object of the present invention to provide a method of treating hair for improved style retention. These and other objects will become readily apparent from the detailed description which follows.

Unless otherwise indicated, all percentages and ratios herein are by weight.

45 SUMMARY OF THE INVENTION

The present invention relates to hair care compositions comprising from about 0.01% to about 10% of a rigid silicone polymer, from about 0.1% to about 99.9% of a volatile carrier or mixtures thereof.

50 DETAILED DESCRIPTION OF THE INVENTION

The essential as well as optional components are described below.

Rigid Silicone Polymer

55 The compositions of the present invention contain at least one rigid silicone polymer which when applied to hair imparts style retention benefits.

The polymers comprise from about 0.01% to about 10% of the composition, preferably from about 0.05% to about 7%.

60 Polymers useful in the present invention include, but are not limited to, filler reinforced polydimethyl siloxane gums including those having end groups such as hydroxyl, cross linked siloxanes such as organic substituted silicone elastomers, organic substituted siloxane gums including those having end groups such as hydroxyl, resin reinforced siloxanes and cross linked siloxane polymers.

The rigid silicone polymers useful in the present invention have complex viscosities of at least 2×10^5 poise (P), preferably about 1×10^7 or more, where complex viscosity is measured by subjecting a sample to

oscillatory shear at a fixed frequency of 0.1 rad/sec at 25°C using a Rheometric Fluids Spectrometer® measuring films having a thickness of about 1 millimeter. The resulting viscous and elastic force responses are combined to determine the complex modulus which is divided by the imposed frequency to compute the complex viscosity.

A preferred siloxane gum is a diphenyl-dimethyl polysiloxane gum useful in the invention has a molecular weight of at least about 500,000, and must be diphenyl substituted to the extent of 3% or more, preferably at least about 5%.

The siloxane gums may be filler reinforced to provide additional rigidity. Silica is the preferred filler.

The silicone elastomer useful in the composition of the present invention is that type of material described in U.S. Patent 4,221,688, September 9, 1980 to Johnson et al, incorporated herein by reference. The actual material described in the patent and what is put into the present compositions is an aqueous emulsion which dries to form an elastomer upon removal of the water.

The silicone emulsion has a continuous water phase in which there is a dispersed phase which comprises an anionically stabilized hydroxylated polyorganosiloxane, a colloidal silica and a catalyst. The pH of the emulsion should be in the range of from about 9 to about 11.5, preferably from about 10.5 to about 11.2. The solids content of the emulsion is generally from about 20% to about 60%, preferably from about 30% to about 50%. The amount of colloidal silica present for each 100 parts by weight of the polydiorganosiloxane is from 1 to 150 parts. On the same basis the amount of diorganotinocarboxylate (e.g., dioctyl tin dilaurate) catalyst is from 0.1 to 2 parts. The elastomer emulsion is used in an amount of from about 0.1% to about 5%, preferably from about 0.5% to about 4% of the total composition.

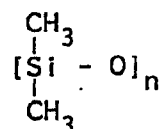
Silicone resins are silicone polymers with a high degree of crosslinking introduced through the use of trifunctional and tetrafunctional silanes. Typical silanes used in the manufacture of resins are monomethyl, dimethyl, monophenyl, diphenyl, methylphenyl, monovinyl, and methylvinyl chlorosilanes, together with tetrachlorosilane. A preferred resin is one offered by General Electric as GE SR545. This resin is provided as a solution in toluene which is stripped prior to the resin's use.

Other rigid silicone polymers of interest are those siloxanes which have been sparingly crosslinked but are still soluble in solvents such as cyclomethicone. Precursors for the rigid material can be any high molecular weight polydimethyl siloxanes, polydimethyl siloxanes containing vinyl groups and other siloxanes. Methods of crosslinking include heat curing with organic peroxides such as dibenzoyl peroxide and di-t-butyl peroxide, heat vulcanization with sulfur and high-energy radiation.

Volatile Carrier

The compositions of the invention comprise a volatile carrier, or mixtures thereof, which preferably is present from about 0.1% to about 99.9% for the silicone polymer. The term "volatile" as used herein means that the material has a measurable vapor pressure.

Where the rigid silicone polymer is a polydimethyl siloxane or a polydiphenyldimethyl siloxane, the preferred carriers are volatile silicones having a boiling point between 99°C to about 260°C and have a solubility in water of less than about 0.1%. The degree of substitution on the siloxane (higher substitution, lower solubility) obviously affects the polymer's solubility and is taken into account by the formulator. The silicones may be either cyclic or linear polydimethyl siloxanes. The number of silicone atoms in the cyclic silicones is about 3 to about 7, most preferably 4 or 5. The general formula for cyclic silicones is:



wherein $n = 3-7$. Viscosities are generally less than 10 centipoise (cP) at 25°C.

Linear polydimethyl siloxanes useful in the invention generally have viscosities of about less than about 5cP at 25°C. The linear volatile silicones contain from about 3 to about 9 silicone atoms and have the general formula



wherein $n = 1-7$.

Silicones of the above described types are widely available e.g., from Dow Corning as 344,345 and 200 fluids; Union Carbide as Silicone 7202 and 7158, and Stauffer Chemical as SWS-03314.

Also useful in compositions of the invention are certain volatile hydrocarbons. These hydrocarbons may be either straight chain or branched, and contain from about 10 to about 16 carbon atoms, preferably from about 12 to about 16 carbon atoms.

Water is also useful in compositions of the present invention either alone or in mixtures with other volatile carriers. Where the elastomer alone is used, water may be preferred and if so, a surfactant, as described below, is also present.

Short chain alcohols such as ethanol are also suitable solvents for use in the present compositions.

Optional Ingredients

Surfactants

5 Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about .05% to about 50%. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25% of the composition. For conditioners the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

10 Synthetic anionic detergents useful herein, particularly for the shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ wherein R is alkyl or alkenyl or about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 12 to 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with 1 to 10, and especially 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

20 Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl triethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to 16 carbon atoms and an average degree of ethoxylation of from about 1 to 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to 20% by weight C_{12-13} compounds; from 60 to 100% by weight of $\text{C}_{14-15-16}$ compounds, from about 0 to 20% by weight of $\text{C}_{17-18-19}$ compounds; from about 3 to 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to 90% by weight of compounds having a degree of ethoxylation of from 1 to 4; from about 10 to 25% by weight of compounds having a degree of ethoxylation of from 4 to 8; and from about 0.1 to 15% by weight of compounds having a degree of ethoxylation greater than 8.

30 Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from 8 to 24, preferably 12 to 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 12 to 18 carbon atoms and a sulfonating agent e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

40 Additional examples of anionic synthetic detergents which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, or example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

45 Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinimate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

50 Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

55 The α -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

60 In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

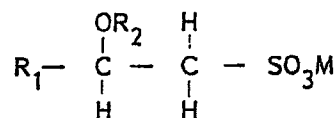
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A specific α -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880 of Phillip F. Pflaumer and Adrian Kessler, issued July 25, 1967, titled "Detergent Composition", the disclosure of which is incorporated herein by reference.

Another class of anionic organic detergents are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 6 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 (preferred) to 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Specific examples of β -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein to provide superior cleaning levels under household washing conditions include: potassium- β -methoxydecylsulfonate, sodium 2-methoxytridecylsulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium β -methoxyoctadecylsulfonate, and ammonium β -n-propoxydodecylsulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCUTCHEON'S, DETERGENTS AND EMULSIFIERS, 1984 ANNUAL, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,878, to Laughlin et al., issued December 30, 1975 discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

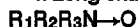
Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R_2 and R_3 contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxy propyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



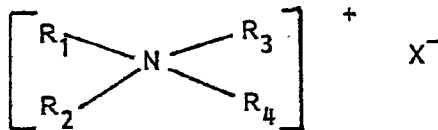
wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hy-

droxypropyldi(2-hydroxyethyl) phosphine oxide, stearyl dimethyl phosphine oxide, cetyl ethyl propyl phosphine oxide, oleyl diethyl phosphine oxide, dodecyl diethyl phosphine oxide, tetradecyl diethyl phosphine oxide, dodecyl dipropyl phosphine oxide, dodecyl di(hydroxymethyl) phosphine oxide, dodecyl di(2-hydroxyethyl) phosphine oxide, tetradecyl methyl-2-hydroxypropyl phosphine oxide, oleyl dimethyl phosphine oxide, 2-hydroxydodecyl dimethyl phosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which contain alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

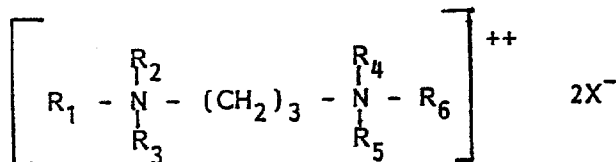
Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactant vehicle materials among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 is hydrogen, an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R_2 is an aliphatic group having from 1 to 22 carbon atoms; R_3 and R_4 are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups.

Other quaternary ammonium salts useful herein are of the formula



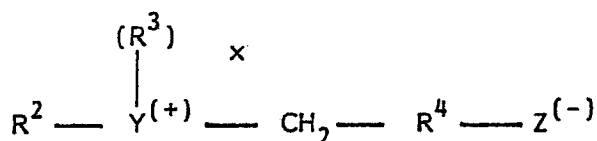
wherein R_1 is an aliphatic group having from 16 to 22 carbon atoms, R_2 , R_3 , R_4 , R_5 and R_6 are selected from hydrogen and alkyl having from 1 to 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein in the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid. (Tallow fatty acids give rise to quaternary compounds wherein R_1 and R_2 have predominately from 16 to 18 carbon atoms.) Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dielcosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant vehicle materials. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl

stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl/behenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate and N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants include among these useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein.)

Zwitterionic surfactants, useful in shampoos as well as conditioners, can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom; R⁴ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]-2-hydroxypropane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxypentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxy-ethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxy-ethyl) carboxy methyl betaine, stearyl bis-(2-hydroxy-propyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl) alpha-carboxyethyl betaine, etc. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxy-ethyl) sulfopropyl betaine and the like; amido betaines and amidosulfobetaines, wherein the RCONH(CH₂)₃ radical is attached to the nitrogen atom of the betaine are also useful in this invention. The amido betaines are preferred for use in some of the compositions of this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, the ethoxylated alkyl sulfates and mixtures thereof are preferred for use herein.

Where the hair care compositions are conditioner compositions, preferred optional components include gel vehicle materials. The vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Such gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems

Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

Lipid vehicle material:

5 The vehicles incorporate one or more lipid materials, (herein referred to as comprising a "lipid vehicle material", singly or in combination) which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from 12 to 22, preferably from 16 to 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

10 Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3d edition, D. Swern, ed. 1979) (incorporated by reference herein). Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published 15 November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-102 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1967 (incorporated by reference herein.)

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Other vehicles, suitable for use with the rigid silicones herein are, for example, tonics, mousses and hairsprays. Tonics utilize a solvent such as water or alcohol while mousses and hairsprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane in addition to the rigid silicone and optional components as set forth below. The level of propellant 25 can be adjusted as desired but is generally from about 3% to about 30% for mousses and from about 15% to about 40% for hairsprays.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more acceptable. Such conventional optional ingredients are well known to those skilled in the art, e.g., pearlescent aids such as ethylene glycol distearate; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers such as a diethanolamide of a long chain fatty acid (e.g. PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose starches and starch derivatives, fatty alcohols such as cetearyl alcohol, sodium chloride, sodium sulfate, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; coloring agents such as any 35 of the FD&C or D&C dyes; hair oxidizing (bleaching) agents such as hydrogen peroxide, perborate and persulfate salts, hair reducing agents such as the thiolglycolates; perfumes; and, sequestering agents such as disodium ethylenediamine tetraacetate, polymer plasticizing agents such as glycerin and propylene glycol. Such agents generally are used individually at a level of from about 0.01% to about 10%, preferably from about 0.05% to about 5.0% by weight of the composition.

40 The pH of the present compositions is not critical and may be in the range of from about 3 to about 10.

As with all compositions, the present compositions should not contain components which unduly interfere with the performance of the compositions.

METHOD OF MANUFACTURE

45 Methods of manufacture of various types of hair care compositions are described in the following examples.

INDUSTRIAL APLICABILITY

The present compositions are used in a conventional manner varying with the type of composition described.

50 The following Examples further illustrate the preferred embodiments within the scope of the present invention. The Examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

55 EXAMPLE 1

Shampoo Compositions

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<u>Component</u>	<u>Weight %</u>	
Ammonium lauryl sulfate	8.59	5
EDTA	0.20	
Citric acid	0.79	10
Sodium hydroxide	0.75	
Cocamide MEA	1.00	
Glycol distearate	1.50	15
Ammonium laureth-3 sulfate	12.09	
Cetearyl alcohol	0.10	
Silicone premix (see examples) ¹		20
Preservative	0.03	
Fragrance	0.30	
Distilled water	q.s.	25

¹: Level of silicone premix varies with selection

Silicone Premixes:	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	
D-5 cyclomethicone	1.50	--	1.50	1.50	30
Polydimethyl siloxane ¹	1.50	--	0.30	--	
Silica ²	0.26	--	--	--	
Silicone elastomer ³	--	3.00	--	--	35
Purified resin ⁴	--	--	0.60	--	
Diphenyldimethyl siloxane gum ⁵	--	--	--	1.50	40

¹: SE-76 gum, supplied by General Electric Company

²: Cab-O-Sil HS-5, supplied by Cabot Corporation 45

³: Silicone elastomer Q3-5205, supplied by Dow Corning Corporation

⁴: SR-545 resin, supplied by General Electric Company 50

⁵: SE54 gum supplied by General Electric Company

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- I: The polydimethyl siloxane and silica are intimately mixed in a high shear ribbon mix for at least 2 hours. The blend is then dissolved in the D-5 cyclomethicone to form the silicone premix.
- II. The silicone elastomer is added directly to the batch.
- III. The resin is received as a solution in toluene. The toluene is stripped completely, and the purified resin is dissolved with the polydimethylsiloxane in the cyclomethicone.

Ammonium lauryl sulfate, EDTA, citric acid, and sodium hydroxide are added to the distilled water at about 15°C. The mixture is heated to from 70°C to 80°C. The cocamide MEA and glycol distearate are added at this point. The ammonium laureth-3 sulfate, cetearyl alcohol and silicone premix are blended at from 70°C to 90°C. This mixture is added to the batch following the glycol distearate. The preservative is then added. The batch is mixed for 5 minutes then cooled to room temperature (15°C to 25°C). The fragrance is added, then the batch is milled under high shear for at least 5 minutes using conventional milling apparatus.

EXAMPLE 2

Mousse Compositions

The following composition was prepared:

	Component	Weight %
30	Luviskol® VA55E (50% active) ¹	9.00
	Propylene glycol	2.00
	Carbopol® 934 ²	0.20
35	Cocodimethyl amine oxide	0.25
	Aminomethyl propanol	0.30
	Glydant® ³	0.37
40	Perfume	0.10
	D.C.Q3-5025 silicone elastomer (40% active) ⁴	2.50
45	A-46 propellant ⁵	10.00
	Double reverse osmosis water	q.s. 100%
	¹ PVP/PVA Copolymer offered by BASF	
50	² Carboxyvinyl polymer offered by B.F. Goodrich Co.	
	³ Preservative offered by Glyco Chemical Co.	
	⁴ Silicone elastomer offered by Dow Corning	
55	⁵ A mixture of propane (20%), Isobutane (78%) and n-butane (2%) offered by Phillips Petroleum Company	

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EMI PA=21 FR=1 HE=40 WI=125 TI=TAB

The aerosol mousses of the present invention are prepared by combining all ingredients except the aerosol propellant into a batch called the concentrate. This concentrate is made by slurring the Carbopol with agitation in the water for several minutes until there are no Carbopol lumps. To this is added the aminomethyl

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propanol while increasing the agitator speed to accommodate the increase in viscosity accompanying neutralization. Maintaining vigorous agitation, the remaining ingredients except for Glydant and silicone elastomer are added and mixed until well dispersed. The Glydant and silicone elastomer are finally added and mixing continued until these are thoroughly dispersed. The resulting concentrate is very thick with a pH of 8.2. Aerosol mousse cans are prepared by placing 135 grams of concentrate into 5 oz. aluminum monobloc (epoxy lining) cans, placing mousse valves on can tops, drawing a vacuum to evacuate can headspace (to remove air), and crimping the valve into place. The propellant (15 grams) is added by pressure filling through the valve stem.

EXAMPLE 3

This is another example of a composition which was prepared.

<u>Component</u>	<u>Weight %</u>	
Luviskol K-30 ¹ (30% active)	2.00	15
Xanthan gum	0.70	
Glydant	0.37	
Nonoxynol-14	1.00	20
D.C. Q3-5024 silicone elastomer (40% active) ²	1.00	
A-70 propellant ³	5.00	25
Double reverse osmosis water	q.s. 100%	
¹ PVP polymer offered by BASF		
² Silicone elastomer offered by Dow Corning		30
³ A mixture of propane and isobutane offered by Phillips Petroleum Company		35

EXAMPLE 4

The following is another mousse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>	
Gantrez® ES 225 ¹ (50% active)	4.00	45
Carbopol 941	0.20	
Aminomethyl propanol	0.80	
Glydant	0.37	
A-46	8.00	50
D.C. Q3-5024 silicone elastomer (40% active)	.50	
Double reverse osmosis H ₂ O	q.s. 100%	55
¹ Copolymer of methylvinyl ether/maleic anhydride offered by GAF		60

EXAMPLE 5Conditioner Compositions

A hair conditioner, according to the present invention, was made comprising:

5		<u>Component</u>	<u>Weight %</u>
		Hydroxyethyl cellulose	0.50
10		Quaternium-18 ¹	0.85
		Dimethicone copolyol ²	0.10
		Cetyl alcohol	1.00
15		Stearyl alcohol	0.75
		Ceteareth-20	0.35
		Stearamidopropyl dimethylamine ³	0.50
20		Glycerol monostearate	0.25
		Citric acid	0.13
		Fragrance	0.20
25		Preservative	0.03
		Rigid silicone premix ⁴ (see examples)	--
		Distilled water	q.s. 100%
30		¹ : Adogen 442-100P, Sherex Chemical Company	
		² : Dow Corning 190 Silicone Surfactant	
		³ : Lexamine S-13, Inolex Corporation	
35		⁴ : Amount varies with type of premix selected	

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Rigid Silicone Premix Examples

		<u>Component</u>	<u>Weight %</u> <u>(total batch)</u>
45		Polydimethylsiloxane ¹	0.30
		Silica ²	0.05
50		D-5 cyclomethicone	1.70
		¹ : SE-76 gum, General Electric Company	
55		² : Cab-O-Sil HS-5, Cabot Corporation	

The polydimethyl siloxane and silica are intimately mixed for at least 4 hours in a high shear ribbon mixer. The resulting blend is dissolved in the cyclomethicone to form the premix used in the base formula.

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<u>Component</u>	<u>Weight %</u> <u>(total batch)</u>
Polydiphenyldimethyl siloxane ¹	0.30
D-5 cyclomethicone	1.70
¹ : SE-54 gum, General Electric Company	

The polydiphenyl dimethyl siloxane is dissolved in the cyclomethicone to form the premix used in the base formula.

In place of the gum, a silicone resin may be used to form another premix.

Hydroxyethyl cellulose is added to the distilled water at a temperature of 15°C to 40°C. This mixture is well dispersed, then heated to a temperature of from 60°C to 90°C. Materials 2 through 8 are added to the batch while the temperature is maintained in this range. The mixture is stirred for approximately 10 minutes, then cooled to approximately 50°C. The remaining materials are added to this temperature. The mixture is milled under high shear for approximately 2 minutes using a conventional milling apparatus, then cooled to room temperature and collected.

EXAMPLE 6

A conditioner composition according to the present invention, is as follows:

<u>Component</u>	<u>Weight %</u>
Hydroxyethyl cellulose	0.50
Quaternium-18	0.40
Dimethicone copolyol	0.10
Cetyl alcohol	1.00
Stearyl alcohol	0.75
Ceteareth-20	0.35
Stearamidopropyl dimethylamine	0.50
Glyceryl monostearate	0.25
Citric acid	0.13
Fragrance	0.20
Preservative	0.03
Silicone elastomer ¹	1.00
Double reverse osmosis water	q.s. 100%

¹: Silicone Elastomer Q3-5205, Dow Corning Corporation

A hair conditioning product, as comprised above, was made in a manner similar to that described in the base formula. This product, when applied to human hair, is useful as a hair conditioner. The silicone elastomer is added directly to the base formula.

EXAMPLE 7

An aerosol hairspray composition of the present invention is as follows:

	<u>Component</u>	<u>Weight %</u>
	A-31 Propellant ¹	75.00
5	SDA40 200 proof ethanol	22.00
	Silicone premix	3.00

	<u>Silicone Premix</u>	<u>Parts</u>
10	Polydimethyl siloxane ²	2.50
	Silica ³	.50
15	1: Isobutane offered by Phillips Petroleum Company	
	2: SE-76 gum, supplied by General Electric Company	
	3: Cab-O-Sil HS-5, Cabot Corporation	

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The polydimethyl siloxane and silica are intimately mixed in a high shear ribbon mixer for at least 4 hours. Aerosol hairspray cans are then prepared by adding 3 grams of silicone premix and 22 grams SDA40 200 proof ethanol to the aerosol can, placing valves on can tops, drawing a vacuum to evacuate can headspace (to remove air), and crimping valves into place. The propellant (75 grams) is added by pressure filling through the valve stem.

A premix containing 1% of the siloxane gum and 2% of purified resin SR545 may be used in place of the above-described premix.

30 EXAMPLE 8

The following is a pump spray tonic composition of the present invention:

	<u>Component</u>	<u>Weight %</u>
35	DIC Q3-5025 silicone	4.00
	Elastomer (40% active)	
	Sodium lauryl sulfate	0.20
40	Glydant	0.37
	Perfume	0.01
	Double reverse osmosis water	q.s. to 100%

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The ingredients are added in order, water, sodium lauryl sulfate, perfume, Glydant, and silicone elastomer. The batch is mixed at ambient temperature for 20 minutes. The batch is then placed in pump bottle.

50 EXAMPLE 9

The following is a styling composition of the present invention:

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<u>Component</u>	<u>Weight %</u>	
SDA 40 ethanol	40.00	
Cyclomethicone (D ₅)	2.00	5
Silicone gum ¹	.05	
Benzoyl peroxide	.00005	
Fragrance	.05	10
Double reverse osmosis water	q.s. 100%	

The silicone premix is prepared by first crosslinking the silicone gum with benzoyl peroxide. This is accomplished by thoroughly blending the benzoyl peroxide into the silicone gum with a ribbon or other suitable mixer. This mixture is then heated to about 150°C for twenty minutes. The result crosslinked gum is then mixed with the cyclomethicone for several hours until it has fully dispersed. 15

The tonic itself is prepared by simply adding the premix to the water, fragrance, and ethanol.

¹: SE76 offered by General Electric

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EXAMPLE 10

The following is another hair tonic composition of the present invention:

<u>Component</u>	<u>Weight %</u>	
Ethanol (SDA 40)	40.0	25
D-4 cyclomethicone±	1.56	
Dimethicone gum ¹	0.013	30
Silica ²	0.0024	
Fragrance	0.20	
Water	q.s. 100%	35
¹ : SE-76 from General Electric		
² : Cab-O-Sil HS-5 from Cabot		40

The silica and dimethicone gum are intimately mixed for at least 2 hours in a high shear ribbon mixer. This compound is then dissolved in the cyclomethicone. This blend is added to the rest of the tonic formula. 45

EXAMPLE 11

The following is another hair tonic composition of the present invention:

<u>Component</u>	<u>Weight %</u>	
Ethanol (SDA 40)	40.0	50
D-5 cyclomethicone	2.0	
Polydiphenyldimethyl siloxane ¹	0.05	55
Fragrance	0.20	
Water	q.s. 100%	
¹ : SE-54, General Electric		60

The polydiphenyl dimethyl siloxane is dissolved in the cyclomethicone. This blend is added to the rest of the tonic formula. 65

EXAMPLE 12

The following is yet another hair tonic composition of the present invention:

	<u>Component</u>	<u>Weight %</u>
5	Fragrance±	0.2
	Ethanol (SDA 40)	30.0
	D-5 cyclomethicone	1.5
10	Dimethicone gum ¹	0.187
	Purified resin SR545 ²	0.375
	Water	q.s.100%
15	¹ : SE-76, General Electric	
	² : The resin is received as a solution in toluene from General	
20	Electric. The toluene is stripped completely, and the purified	
	resin is dissolved at 50% in cyclomethicone. The dimethicone is	
	also dissolved in a separate solution with cyclomethicone. The	
25	two solutions are blended together. This mixture is added to the	
	rest of the formula.	

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Claims

- 35 1. A hair care composition comprising:
a) from about 0.01% to about 10% of a rigid silicone polymer having a complex viscosity of at least 2×10^5 poise; and
b) a volatile carrier
wherein if water is the sole carrier a surfactant is also present.
- 40 2. A hair care composition according to Claim 1 wherein the rigid silicone polymer is selected from the group consisting of organic substituted siloxane gums, silicone elastomers, filler reinforced dimethyl siloxane gums, resin reinforced siloxanes and crosslinked siloxane polymers.
3. A hair care composition according to Claims 1 or 2 wherein the volatile carrier is a cyclic silicone containing from about 3 to about 7 silicon atoms.
- 45 4. A hair care composition according to Claim 1 or 2 wherein the volatile carrier is water.
5. A hair care composition according to Claims 1, 2 or 4 in the form of a shampoo which additionally contains a synthetic surfactant.
6. A hair care composition according to Claim 5 wherein the rigid silicone polymer is a silica reinforced dimethyl siloxane gum.
- 50 7. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a conditioner.
8. A hair care composition according to Claim 7 which in addition contains a lipid material and a cationic surfactant.
9. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a hair tonic.
10. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a hairspray.
- 55 11. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a mousse.
12. A hair care composition comprising:
a) from about 0.05% to about 70% of a rigid silicone polymer selected from the group consisting of filler reinforced polydimethylsiloxane polymers, silicone elastomers and polydiphenyl-dimethyl siloxane polymers; and
b) a volatile carrier.
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(54) Title: HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER (57) Abstract Liquid hair styling composition useful for spray application to hair which comprises: (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000; (b) a liquid vehicle selected from the group consisting of water, C ₁ -C ₆ monohydric alcohols, and mixtures thereof; (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier; said composition having a pH of about 10 or less. In yet another aspect of this invention, provided are reduced volatile organic solvent hair spray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C ₁ -C ₆ monohydric alcohols, wherein said composition comprises at least about 10 %, by weight, water.		

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HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER

5

TECHNICAL FIELD

10 The present invention relates to hair spray compositions which comprise a high molecular weight hair styling polymer. More particularly, this invention relates to hair spray compositions containing high molecular weight hair styling polymer and having improved sprayability.

BACKGROUND OF THE INVENTION

15 The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or hair "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or
20 by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style
25 retention is typically achieved by the use of resins, such as AMPHOMER, supplied by National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hair spray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000. When such resins are incor-
30 porated into pump and aerosol hair sprays, they can provide a combination of suitable style retention and good sprayability. "Sprayability" refers to the spray quality and pattern. Good sprayability for hair spray formulations is characterized by a wide spray pattern without a wet, drippy center, and by suf-
35 ficiently small droplet size to provide a fine mist.

- 2 -

It remains desirable, however, to provide hair spray compositions that have improved hold and style retention performance. One technique for providing improved style retention for liquid hair spray compositions would be to utilize higher molecular weight hair styling resin. Alternately, this could reduce the amount of resin needed to provide a particular level of style retention. High molecular weight hair styling polymers, when utilized commercially, have typically been formulated as gels, lotions, or other non-spray compositions. Unfortunately, high molecular weight resins in liquid hair spray formulations tend to suffer from poor sprayability. More specifically, such formulations tend to have spray quality characterized by reduced spray pattern diameter, increased incidence of wet, drippy centers, and a tendency toward larger droplet size or streaming upon spraying, as opposed to a fine mist. This can result in overly heavy concentrations of hair spray in regions of the hair, causing the hair to be too stiff in those regions, whereas other areas may have too little hair spray applied and, consequently, have poor style retention and hold.

Thus, it is an object of this invention to provide liquid hair spray compositions utilizing high molecular weight styling resins that can provide improved style retention and retain good sprayability characteristics.

Recently, it has been found that certain polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al.,

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issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319*, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320*, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

Whereas these silicone macromer-containing hair styling polymers can provide good overall hair styling performance with a desirable hair conditioning effect, they are preferably used in hair spray at relatively high molecular weights, compared to most commercial products (although they can also be used at more conventional hair spray resin molecular weights (eg., about 50,000 to about 150,000 weight average molecular weight). Furthermore, they are difficult to formulate into a hair spray composition with good sprayability characteristics.

Therefore, it is another object of this invention to provide liquid hair spray compositions containing high molecular weight silicone-containing hair styling polymers which have improved spray characteristics.

It is also desirable to formulate hairspray compositions with reduced levels of volatile organic solvents, e.g., ethanol, propanol, etc. One way to do this is to increase the amount of water present in the composition at the expense of the volatile organic solvent. Unfortunately, this tends to adversely affect hairspray performance, especially drying time upon application, spray quality, and hair feel. This is particularly a problem for reduced volatile organic solvent compositions utilizing silicone macromer-containing hair setting resins. It is especially difficult to obtain good spray quality and hair feel from high water content compositions.

It is yet another object of this invention to obtain improved hairspray compositions containing silicone macromer-containing hair setting resins having reduced volatile organic solvents.

These and other objects as may be apparent to one skilled in the art can be obtained by the invention hereof, which is described in the description which follows. Unless otherwise indicated (*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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licated, all percentages and ratios herein are by weight.

SUMMARY OF THE INVENTION

5 The present invention provides improved sprayability hair spray compositions with high molecular weight hair styling polymers that can provide excellent hair styling/hold benefits upon spray application to the hair.

10 According to the present invention, sprayability of high molecular weight polymers can be improved through the use of ionic strength modifier systems consisting essentially of mixtures of non-surface active anions and cations. It is an essential aspect of the invention that the hair styling polymer also be of an ionic character.

15 More specifically, the present invention relates to a liquid hair styling composition useful for spray application to hair which comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆, preferably C₂-C₄, monohydric alcohols, and mixtures thereof;
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier;

said composition having a pH of about 10 or less.

30 In one aspect of the invention, the high molecular weight hair styling polymer can be any of the conventional classes of hair styling or hair setting polymers in the art, i.e., polymers free of silicone portions.

35 In another aspect of the invention, the high molecular weight polymer is a silicone macromer-containing hair setting polymer that can provide hair styling and hold benefits while also providing improved softness to the hair relative to non-silicone-containing polymers. In yet another aspect of this

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invention, provided are reduced volatile organic solvent hairspray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C_1 - C_6 , preferably C_2 - C_4 , monohydric alcohols, wherein said composition comprises at least about 10%, by weight, water.

DETAILED DESCRIPTION OF THE INVENTION

The essential as well as various optional components are described below.

Hair Styling Polymer

The compositions of the present invention contain an effective amount of a high molecular weight hair styling polymer to impart styling benefits upon application to hair. As used herein, "hair styling polymer" means any polymer, natural or synthetic, that can provide hair setting benefits. Polymers of this type are well known in the art. Generally, the level of hair styling polymer used will be at least about 0.1%, by weight, of the composition. Typically, it will be present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 8%.

The hair styling polymers hereof also are of ionic character. As used herein, "ionic hair styling polymer", or the term "ionic character" in reference to hair styling polymers or monomers of which such hair styling polymers are comprised, means hair styling polymers that are anionic, cationic, amphoteric, zwitterionic, or otherwise can exist in the liquid vehicle of the hair styling composition in dissociated form.

Any type of ionic hair styling polymer which is soluble or dispersible in the liquid carrier can be used in the present invention. A wide variety of such types of hair styling polymers are known in the art.

The ionic hair styling polymers hereof can be homopolymers, copolymers, terpolymers, etc. As used herein, the term "polymer" shall encompass all of such types of polymeric materials.

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As an essential aspect, the polymers hereof must comprise monomers of an ionic character. For convenience in describing the polymers hereof, monomeric units present in the polymers may be referred to as the monomers from which they can be derived. The ionic monomers can be derived from polymerizable ionic starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to be of ionic character. Also included are corresponding salts, acids and bases of the monomers exemplified.

Examples of anionic monomers include:

(i) unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid;

(ii) half esters of an unsaturated polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate and, hydroxyethyl methacrylate, hydroxypropyl acrylate and the like;

(iii) monomers having a sulfonic acid group such as styrene-sulfonic acid, sulfoethyl acrylate and methacrylate, and the like; and

(iv) monomers having a phosphoric acid group such as acid phosphoxyethyl acrylate and methacrylate, 3-chloro-2-acid phosphoxypropyl acrylate and methacrylate, and the like.

Examples of the cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloxypropyltrimethylammonium chloride and (meth)acryloxypropyltriethylammonium bromide;

(ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C₁-C₄ alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or

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dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by
(1) neutralization with an acid such as hydrochloric acid, or
lactic acid, (2) modification with a halogenated alkyl, such as
5 methyl chloride, ethyl chloride, methyl bromide, or ethyl iodide,
(3) modification with a halogenated fatty acid ester such as ethyl
monochloroacetate, or methyl monochloropropionate, and (4)
modification with a dialkyl sulfate such as dimethyl sulfate, or
diethyl sulfate.

10 Furthermore, the cationic unsaturated monomers include amine
derivatives of allyl compounds such as diallyldimethylammonium
chloride and the like.

These cationic unsaturated monomers can be polymerized in
cationic form, or as an alternative they can be polymerized in the
15 form of their precursors, which are then modified to be cationic,
for example, by a quaternizing agent (e.g. ethyl monochloro-
acetate, dimethyl sulfate, etc.).

Examples of the amphoteric monomers include zwitterionized
derivatives of the aforementioned amine derivatives of (meth)-
20 acrylic acids or the amine derivatives of (meth)acrylamide such as
dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acryl-
amide by a halogenated fatty acid salt such as potassium mono-
chloroacetate, sodium monobromopropionate, aminomethylpropanol
salt of monochloroacetic acid, triethanolamine salts of mono-
25 chloroacetic acid and the like; and amine derivatives of (meth)-
acrylic acid or (meth)acrylamide, as discussed above, modified
with propanesultone.

These amphoteric monomers, like the aforementioned cationic
monomers, can be polymerized in amphoteric form or, as an alterna-
30 tive, they can also be polymerized in the form of their pre-
cursors, which are then converted into the amphoteric state.

Preferred ionic monomers include acrylic acid, methacrylic
acid, dimethylaminoethyl methacrylate, quaternized dimethyl-
aminoethyl methacrylate, maleic acid, maleic anhydride half
35 esters, crotonic acid, itaconic acid, diallyldimethyl ammonium
chloride, polar vinyl heterocyclics such as vinyl imidazole, vinyl

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pyridine, styrene sulfonate, and mixtures thereof. Especially preferred ionic monomers include acrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, and mixtures thereof.

5 Salts of acid and amine monomers listed above can also be used, e.g., sodium, potassium, or other alkali or alkaline earth metal salts.

10 The polymers hereof should contain at least about 1%, by weight, ionic monomer, preferably at least about 2%, more preferably at least about 5%.

 The hair styling polymers hereof can also contain nonionic monomers including, both high polarity monomers and low polarity monomers.

15 The ionic polymers hereof will generally comprise from about 1% to 100% ionic monomers and from 0% to about 99% nonionic monomers, preferably from about 2% to about 75% ionic monomers and from about 25% to about 98% nonionic monomers, more preferably from about 5% to about 50% ionic monomers and from about 50% to about 95% nonionic monomers.

20 Representative examples of low polarity nonionic monomers are acrylic or methacrylic acid esters of C₁-C₂₄ alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-24
25 carbon atoms with the average number of carbon atoms preferably being from about 4-18, more preferably from about 4-12; styrene; chlorostyrene; vinyl esters such as vinyl acetate; vinyl chloride; vinylidene chloride; acrylonitrile; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl
30 toluene; alkoxyalkyl (meth)acrylate, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and mixtures thereof. Other
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nonionic monomers include acrylate and methacrylate derivatives such as allyl acrylate and methacrylate, cyclohexyl acrylate and methacrylate, and methacrylate, oleyl acrylate and methacrylate, benzyl acrylate and methacrylate, tetrahydrofurfuryl acrylate and methacrylate, ethylene glycol di-acrylate and -methacrylate, 1,3-buteneglycol di-acrylate and -methacrylate, diacetoneacrylamide, isobornyl (meth)acrylate, and the like.

Preferred nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative polar nonionic monomers include acrylamide, N,N-dimethylacrylamide, methacrylamide, N-t-butyl acrylamide, methacrylonitrile, acrylamide, acrylate alcohols (e.g. C₂-C₆ acrylate alcohols such as hydroxyethyl acrylate and hydroxypropyl acrylate), methacrylate, and hydroxypropyl methacrylate, vinyl pyrrolidone, vinyl ethers, such as methyl vinyl ether, acyl lactones, vinyl pyridine, allyl alcohols, vinyl alcohols and vinyl caprolactam.

Examples of anionic hair spray polymers are copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; and copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated aliphatic alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers and terpolymers containing acrylic acid or methacrylic acid as the anionic radical containing moiety such as copolymers with methacrylic acid, butyl acrylate, ethyl methacrylate, etc. Another example of an acrylic polymer which can be employed in the compositions of the present invention is a polymer of tertiary-butyl acrylamide, acrylic acid, and ethyl acrylate.

An example of an amphoteric polymer which can be used in the present invention is Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer, described generally in U.S. Pat. No.

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4,192,861 as being a polymer of N-tert-octyl acrylamide, methyl methacrylate, hydroxypropyl methacrylate, acrylic acid and t-butyl aminoethyl methacrylate, of appropriate molecular weight for purposes hereof.

5 Examples of cationic hair spray polymers are copolymers of amino-functional acrylate monomers such as lower alkylamino alkyl acrylate or methacrylate monomers such as dimethyl aminoethyl-methacrylate with compatible monomers such as N-vinylpyrrolidone or alkyl methacrylates such as methyl methacrylate and ethyl
10 methacrylate and alkyl acrylates such as methyl acrylate and butyl acrylate. Cationic polymers containing N-vinylpyrrolidone are commercially available from GAF Corp.

15 Still other organic, ionic hair styling polymers include carboxymethyl cellulose, copolymers of PVA and crotonic acid, copolymers of PVA and maleic anhydride, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer, monoethyl ester of poly(methyl vinyl ether-maleic acid), and octylacrylamide/acrylate/butylaminoethyl
20 methacrylate copolymers. Mixtures of polymers may also be used.

Silicone-Containing Hair Styling Polymers

Preferred ionic hair styling polymers are silicone-containing polymers. Ionic silicone macromer-containing polymers are described, for example, in EPO Application 90307528.1,
25 published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March
30 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319,* Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320,* Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

35 Examples of useful polymers and how they are made are also (*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

5 Preferred ionic silicone macromer-containing polymers comprise an organic polymeric backbone, preferably a vinyl backbone, having a Tg above about -20°C (more preferably above about 20°C) and, grafted to the backbone, a siloxane macromer having a weight
10 average molecular weight of preferably at least about 500 preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. In addition to the graft copolymers described above, silicone-containing polymers also include block copolymers preferably containing up to about 50% (more preferably from about 10% to about 40%) by weight of one
15 or more siloxane blocks and one or more non-silicone blocks (such as acrylates or vinyls).

The silicone macromer-containing polymers preferred for use herein are such that when formulated into the finished hair care composition, and dried, the polymer phase separates into a dis-
20 continuous phase which includes the silicone portion and a continuous phase which includes the organic portion.

The silicone macromer-containing ionic hair styling polymers generally comprise nonionic silicone-containing monomers together with ionic monomers as described above, and can also contain
25 non-silicone-containing nonionic monomers, also described above. The silicone-containing monomers also can be ionically charged and, as such, contribute, in part or in whole, to the overall charge density of the polymer.

The silicone-containing hair styling polymers hereof will
30 generally comprise about 0.01% to about 50% of silicone-containing monomer, preferably from about 0.5% to about 40%, more preferably from about 2% to about 25%.

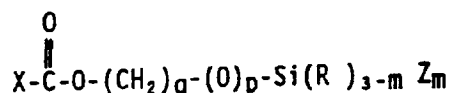
The silicone-containing monomer will generally have the formula:

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$$X(Y)_nSi(R)_3-mZ_m$$

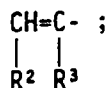
wherein X is a vinyl group copolymerizable with the other monomers

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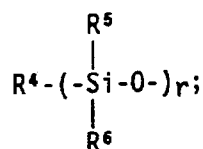
of the polymer; Y is a divalent linking group; R is a hydrogen, lower alkyl (eg. C₁-C₄), aryl, alkaryl, alkylamino, or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, and is pendant from the organic polymeric backbone; n is 0 or 1; and m is an integer from 1 to 3. Of course, Z should be essentially unreactive under polymerization conditions. The silicone-containing monomer preferably has a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably from about 5,000 to about 20,000. Preferably, it is of the formula:



wherein m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is



R³, R⁴, R⁵, R⁶ independently are alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen, or hydroxyl (preferably alkyl, more preferably methyl); and r is an integer of at least about 10, preferably from about 5 to about 1500 (more preferably r is from about 75 to about 700, most preferably from about 100 to about 250. Particularly preferred are monomers when p=0 and q=3.

The silicone-containing monomers of the ionic polymers hereof can be polymerized in a silicone-containing monomer form. Alternatively, they can be polymerized in the form of their non-silicone containing precursor, and a silicone group can then be added. For example, carboxylate-containing monomers, such as acrylic

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acid, can be polymerized and then reacted with a silicone-containing compound with a terminal epoxy group. The result will, in general, be a silicone-containing monomer in the polymer having an equivalent structure to the formula $X(Y)_nSi(R)_{3-m}Z_m$, described above, and is intended to be encompassed herein.

5 The preferred silicone-containing polymers useful in the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of nonionic monomer, from 1% to about 98% (preferably from about 15% to about 80%) of ionic monomer, with from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of the monomers being
10 silicone-containing monomer. The combination of the non-silicone-containing monomers preferably is from about 50% to about 99% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer.
15

Exemplary silicone-containing polymers for use in the present invention include the following:

- (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer-20,000 molecular weight
- 20 (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight
- (iii)t-butylacrylate/acrylic acid/PDMS macromer-10,000
25 molecular weight
- (iv)t-butylacrylate/acrylic acid/PDMS macromer-10,000
molecular weight

The ionic hair styling polymers, including both silicone-containing and non-silicone containing polymers, having carboxylate or other acidic functionalities will preferably be
30 utilized in at least partially neutralized form in the compositions hereof to promote solubility or dispersibility of the polymer in the vehicle. In addition, use of the neutralized form aids in shampoo removability of the hair spray compositions. In general, it is preferred that from about 10% to 100%, more
35 preferably from about 20% to about 90%, even more preferably from

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about 40% to about 85%, of the acidic monomers of the polymer be neutralized.

Any conventionally used base, organic or metallic, may be used for neutralization of acidic polymers. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use in the present hair spray compositions. It will be recognized by those skilled in the art that various of the cations supplied neutralizing the polymer will also contribute to the ionic strength modifier system, as described herein.

Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide.

Examples of other suitable neutralizing agents which may be included in the hair spray compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amine-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), moniospropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS). Particularly useful for neutralization are mixtures of amines and metallic bases.

Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrogen chloride.

Liquid Vehicle

The hair spray compositions of the present invention also include a liquid vehicle. This can comprise any of those conventionally used in resin hair spray formulations. The liquid vehicle is present in the hair spray compositions at from about 80% to about 99%, preferably from about 85% to about 99%. More preferably, the liquid vehicle is present at from about 90% to about 98% of the total composition.

Organic solvents suitable for use in the liquid vehicle of the present compositions are C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present

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compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof. Water is also a preferred solvent for use in the liquid vehicle of the present hair spray compositions.

5 Preferably, the liquid vehicle for the present compositions is selected from the group consisting of C₁-C₆ alkanols, water, carbitol, acetone and mixtures thereof. More preferably, the liquid vehicle of the present composition is selected from the group consisting of water and C₂-C₄ monohydric alcohols such as
10 ethanol and isopropanol, and mixtures thereof.

 In general, water may be absent from the liquid vehicle or may comprise all of the liquid vehicle. Most preferably, the liquid vehicle is a mixture of water and organic solvents.

 Where water and organic solvent mixtures are used, for
15 instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the organic solvents are generally present in the range of from 0.5% to about
20 99%, preferably from about 50% to about 95%, by weight of the total composition.

 In one aspect of the invention, the hair setting resin is of particularly high weight average molecular weight, i.e. weight average molecular weight above about 300,000, especially above
25 about 500,000. It has been found that surprisingly effective hair spray performance can be obtained using these high molecular weight resins in combination with ionic strength modifier system. This invention is especially effective at providing the resins with characteristics in hair spray compositions such that they can
30 be sprayed with good spray quality, especially with respect to silicone macromer-containing hair setting resins, which are preferably used at relatively high molecular weights.

 In another aspect of the invention, what is provided is a low volatile organic solvent hairspray composition which comprises a
35 silicone macromer-containing ionic hair setting resin, an ionic strength modifier system as described herein, and a liquid

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vehicle. A reduced volatile organic solvent hair spray composition of the present invention comprises no more than 80% volatile organic solvents (which include, for purposes hereof, volatile silicone fluids and excludes water). In other embodiments hereof, the hair spray compositions can comprise no more than about 65%, 55%, 50%, or other levels of volatile organic solvents, as may be chosen by product formulators. In the reduced volatile organic solvent hair spray products hereof, the hair spray compositions comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water. The weight average molecular weight of the silicone macromer-containing hair setting resins can be of any level suitable for providing effective hair styling. Typically, it will be at least about 50,000, more typically at least about 70,000, preferably at least about 100,000. As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the more preferred embodiments of this aspect of the invention, the weight average molecular weight of the resin is from about 70,000 to about 1,000,000, most preferably from about 100,000 to about 750,000.

In general, the reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60%, even more preferably up to about 50% water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvents. It is also specifically contemplated that the compositions can be limited to no more than other maximum limits on volatile organic solvents, eg., no more than about 75%, 65%, or 55%, etc..

In general, for the compositions hereof, the weight average molecular weight of the styling polymer is limited only by practical concerns. Generally, it will be below about 10,000,000, preferably below about 3,000,000, more preferably below about 1,000,000.

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Ionic Strength Modifier System

The compositions of the present invention include, as an essential element, an effective amount of an ionic strength modifier system for reducing the viscosity of the hair styling composition, relative to the same composition absent the ionic strength modifiers. In general, the present compositions will comprise at least about 0.01%, by weight, of the ionic strength modifier. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the hair styling polymer will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, hair styling polymer, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched organic hetero-chain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus,

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basic and acidic ions OH^- and H^+ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but they must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, eg., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, eg. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, amino-methylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions

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that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, eg., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The compositions hereof have a water-equivalent pH of about 10 or less, preferably from about 3 to about 10, more preferably from about 5 to about 10. For purposes hereof, water-equivalent pH shall correspond to the pH of a composition containing all of the components of the composition, except that any non-aqueous component of the carrier is replaced by an equal weight of double reverse osmosis (DRO) water.

A preferred reduced volatile organic solvent hairspray composition of the present invention contains from about .01% to about 2% of a fluorosurfactant; from about 0.1% to about 15% of an ionic resin, including those having a weight average molecular weight of 300,000 and above, as well as those below 300,000, and also including those having silicone macromer portions as well as those without; an ionic strength modifier system as described herein, and a liquid vehicle comprising about 10% to about 45%, by weight of the composition water and about 50% to about 80%, by weight of the composition, of an organic solvent, preferably selected from the group consisting of ethanol, isopropanol and mixtures thereof.

The level of ionic strength modifier system used, in general, is given above. It is to be recognized, however, that the particular level of ionic strength modifier system which must be used to achieve an improvement in hair spray performance, or to achieve optimum performance, for a particular hair spray composition can vary depending upon a variety of factors, including the particular type of resin chosen and its molecular weight, and level in the composition, the specific ionic strength modifier system, the level of water and the type and level of volatile organic solvent, and the presence of optional components in the system. In gene-

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ral, higher levels of ionic strength modifier system may be needed to achieve a performance benefit as resin molecular weight and/or water levels are reduced. In general, the compositions hereof should contain at least an effective amount of the ionic strength modifier system provide an improvement in hair feel for a given level of hair hold performance or for improved spray quality (?).

Optional Ingredients

In addition to the ionic strength modifier system described above, the compositions hereof can optionally contain other materials to improve sprayability of the compositions. In particular, it is contemplated to utilize ionic surfactants in combination with the non-surface active anions and cations of the ionic strength modifier system hereof.

A wide variety of surfactants may be advantageously incorporated into the compositions hereof. These include anionic, cationic, amphoteric, and zwitterionic surfactants, and further include both fluorinated surfactants, as described below, and nonfluorinated surfactants.

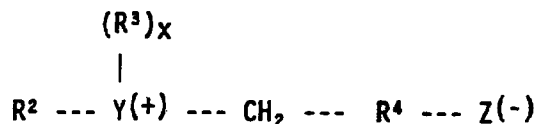
Anionic surfactants include, for example: alkyl and alkenyl sulfates; alkyl and alkenyl ethoxylated sulfates; (preferably having an average degree of ethoxylation of 1 to 10), succinamate surfactants, such as alkylsulfosuccinamates and dialkyl esters of sulfosuccinic acid; neutralized fatty acid esters of isethionic acid; and alkyl and alkenyl sulfonates, including, for example, olefin sulfonates and beta-alkoxy alkane sulfonates. Preferred are alkyl and alkenyl sulfates and alkyl and alkenyl ethoxylated sulfates such as the sodium and ammonium salts of C_{12} - C_{18} sulfates and ethoxylated sulfates with a degree of ethoxylation of from 1 to about 6, preferably from 1 to about 4, e.g., lauryl sulfate and laureth (3.0) sulfate.

Amphoteric surfactants include those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate,

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phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, N-alkyl-
 5 taurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378. Others include alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphoglycinates; alkyl, preferably C₆-C₂₂
 10 and most preferably C₈-C₁₂, amphopropionates; and mixtures thereof.

Suitable zwitterionic surfactants for use in the present compositions can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals
 15 can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:
 20



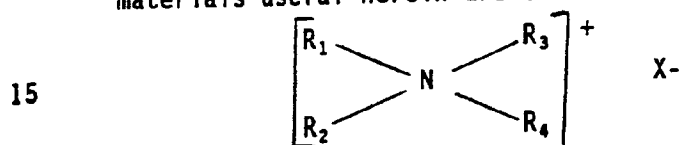
wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of
 25 from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is sulfur or phosphorus, 1 or 2 when Y is nitrogen; R⁴ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups. Classes of zwitterionics include alkyl amino sulfonates, alkyl betaines, and alkyl amido betaines.
 30

35 Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moi-

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eties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Pat. No. 3,155,591, Hilfer, issued Nov. 3, 1964; U.S. Pat. No. 3,929,678, Laughlin, et al., issued Dec. 30, 1975; U.S. Pat. No. 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Pat. No. 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 is an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R_2 is an aliphatic group having from 1 to 22 carbon atoms; R_3 and R_4 are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups. Other quaternary ammonium salts useful herein are diquaternary ammonium salts.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein in the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid. (Tallow fatty acids give rise to quaternary compounds wherein R_1 and R_2 have predominately from 16 to 18 carbon atoms.)

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactants for use herein. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl

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amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl-behenylamine. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Pat. No. 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein).

Suitable cationic surfactant salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts.

Nonionic surfactants can also be included in the compositions hereof. Preferably, the nonionic surfactants have an average HLB (Hydrophile-Lipophile Balance) of less than or equal to about 7.

Methods of determining HLB are well known in the art and any of such methods may be used for HLB determination. A description of the HLB System and methods for HLB determination are described in "The HLB System: a time saving guide to emulsifier selection," ICI Americas Inc.; Wilmington, Delaware; 1976.

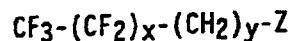
Nonionic surfactants include polyethylene oxide condensates of alkyl phenols (preferably C₆-C₁₂ alkyl, with a degree of ethoxylation of about 1 to about 6), condensation products of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, condensation products of aliphatic alcohols with ethylene oxide, long chain (i.e., typically C₁₂-C₂₂) tertiary amine oxides, long chain tertiary phosphine oxides, dialkyl sulfoxides containing one long chain alkyl or hydroxy alkyl radical and one short chain (preferably C₁-C₃) radical, silicone copolyols, and C₁-C₄ alkanol amides of acids having a C₈-C₂₂ acyl moiety.

Fluorosurfactants (i.e., fluorinated surfactants) useful in the present compositions can be linear or branched alkyl, alkenyl or alkylaryl fluorohydrocarbons having a chain length of preferably 3 to 18 carbon atoms and being fully or partially fluorinated. The hydrophilic moiety can be, for example, sulfate,

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phosphate, phosphonate, sulfonate, amine, amine salts, quaternary ammonium, carboxylate, and any combination thereof. Also, there can be a bridging moiety between the hydrophilic and hydrophobic moieties, such as an amido alkalene group for example.

5 Ionic fluorosurfactants useful in the present compositions include perfluorinated compounds represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 10 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated 15 compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference. 20

Cationic fluorosurfactants preferred for use in the present compositions include fluorinated alkyl quaternary ammonium salts having a variety of anionic counter ions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably 25 an iodide; and those fluorosurfactants conforming to the formula $\text{R}_f\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3[\text{CH}_3\text{SO}_4]^-$ wherein $\text{R}_f=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$, such as ZONYL FSC supplied by E. I. DuPont deNemours and Company (Wilmington, Delaware, USA; DuPont). A preferred fluorinated alkyl quaternary ammonium iodide is FLUORAD FC-135 supplied by Minnesota Mining & Manufacturing (St. Paul, Minnesota, USA; 3M). 30

Anionic fluorosurfactants preferred for use in the present compositions are mono-, and bis-perfluoroalkyl phosphates, such as ZONYL FSP supplied by DuPont and conforming to the general formulae 35 $(\text{R}_f\text{CH}_2\text{CH}_2\text{O})\text{P}(\text{O})(\text{ONH}_4)_2$ and $(\text{R}_f\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})(\text{ONH}_4)$ wherein $\text{R}_f=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$; mono- and bis-fluoroalkyl phosphates, having a

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variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as ZONYL FSJ supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as ZONYL TBS supplied by DuPont and conforming to the formula $R_fCH_2CH_2SO_3X$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and $X=H$ or NH_4 ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as ZONYL RP supplied by DuPont; amine perfluoroalkyl sulfonates, such as FLUORAD FC-99 supplied by 3M; ammonium perfluoroalkyl sulfonates, such as FLUORAD FC-93, FLUORAD FC-120 and L-12402, supplied by 3M; potassium perfluoroalkyl sulfonates, such as FLUORAD-95 and FLUORAD FC-98 supplied by 3M; potassium fluorinated alkyl carboxylates, such as FLUORAD FC-129 and FLUORAD FC-109 supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143[®] supplied by 3M; and those fluorosurfactants conforming to the general formula $R_fCH_2CH_2SCH_2CH_2CO_2Li$ wherein $R_f=F(CF_2CF_2)_{3-8}$, such as ZONYL FSA supplied by DuPont.

Preferred anionic fluorosurfactants are mixed mono- and bis-perfluoroalkyl phosphates, ammonium salts; mixed mono- and bis-fluoroalkyl phosphate, ammonium salts, complexed with aliphatic quaternary methosulfates; perfluoroalkyl sulfonic acid, ammonium salts; mixed telomer phosphate diethanolamine salts; amine perfluoroalkyl sulfonates; ammonium perfluoroalkyl sulfonates; potassium perfluoroalkyl sulfonates; potassium fluorinated alkyl carboxylates; ammonium perfluoroalkyl sulfonates; and ammonium perfluoroalkyl carboxylates.

Amphoteric fluorosurfactants preferred for use in the present compositions are fluorinated alkyl amphoteric surfactants available commercially as FLUORAD FC-100 from 3M.

Zwitterionic fluorosurfactants preferred for use in the

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present compositions are those fluorosurfactants conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ such as ZONYL FSK supplied by DuPont.

5 Preferably, mixtures of amphoteric or zwitterionic fluorosurfactants with anionic fluorosurfactants or mixtures of anionic and cationic fluorosurfactants are used.

The use of fluorosurfactants is especially desirable in reduced volatile organic solvent compositions, and most especially those with silicone macromer-containing polymers.

10 Surfactants are preferably included in the compositions at a level of from about 0.01% to about 2%, more preferably from about 0.01% to about 1.5%, most preferably from about 0.01% to about 1%.

Plasticizer

15 The performance of the hair styling polymers can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at a plasticizer: styling polymer weight ratio of about 1:20: to about 1:1, preferably from about 1:15 to about 20 1:2. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapor pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the volatile carrier is evaporating, since this may 25 excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, 30 second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and Joseph R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982), both incorporated herein by reference. See especially in the Appendix 35 of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

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Plasticizers include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄-C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutgrates, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates, oleates, camphor, and castor oil, and silicone copolyols.

Examples of adipate plasticizers include adipic acid derivatives such as diisobutyl adipate, bis(2-ethylhexyl) adipate, diisodecyl adipate, bis(2-butoxyethyl) adipate, and di-n-hexyl adipate.

Examples of phthalate plasticizers include phthalic acid derivatives such as dibutyl phthalate, butyl octyl phthalate, di-n-octyl phthalate, diisooctyl phthalate, bis(2-ethylhexyl) phthalate, n-octyl n-decyl phthalate, di-n-hexyl phthalate, isooctyl isodecyl phthalate, diisodecyl phthalate, ditridecyl phthalate, butyl cyclohexyl phthalate, butyl benzyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, isodecyl benzyl phthalate, and bis(2-butoxyethyl) phthalate.

Isophthalate plasticizers include bis(2-ethylhexyl) isophthalate.

Examples of azelate plasticizers include azelaic acid derivatives such as di(2-ethylhexyl) azelate, and bis(2-ethylhexyl) azelate.

Examples of stearate plasticizers include stearic acid derivatives such as n-butyl stearate, butyl acetoxystearate, and butoxyethyl stearate.

Examples of citrate plasticizers include citric acid derivatives such as acetyl tri-n-butyl citrate, tri-n-butyl citrate, and acetyl tri-2-ethylhexyl citrate.

Examples of trimellitate plasticizers include tri-(2-ethylhexyl) trimellitate, and triisooctyl trimellitate.

Other examples of plasticizers include dibutyl carbonate, butyl oleate, n-butyl, butyrate, isobutyl butyrate, isopropyl

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butyrate, dibutyl carbonate, ethyl palmitate, isooctyl palmitate, methyl ricinoleate, butyl ricinoleate, diisooctyl sebacate, triisobutyl phosphate, isodecyl pelargonate, ethyl valerate, isocetyl alcohol, octododecanol, isopropyl myristate, isostearyl alcohol and methyl alkyl silicones having C_2-C_{20} alkyl and from 1 to about 500 siloxane monomer units, silicone copolyols, eg. dimethicone copolyol.

Hair Spray Compositions

Hair spray compositions of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas.

The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

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Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

5 Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both
10 incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON
15 AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other Ingredients

The hair spray formulations of the present invention can
20 optionally contain a variety of other hair spray adjuvants as are known in the art. Generally, the compositions will comprise from about 0.05% to 5%, by weight, preferably from about 0.1% to 3%, by weight, of adjuvants. Hair spray adjuvants include: silicones; emollients; lubricants and penetrants such as various lanolin
25 compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints and other colorants; sunscreens; and perfume.

METHOD OF USE

The hair spray compositions of the present invention are used
30 in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits
35 desired considering the length and texture of the hair.

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The following Examples illustrate the present invention. The Examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXAMPLES

Examples I-XVI

Hair spray compositions of the present invention are prepared according to the following formulations.

		Example # (Weight Percent)							
		<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>
	<u>Ingredient</u>								
	Ethanol, 200 proof	79.3	79.3	79.2	79.2	79.1	79.1	79.2	79.2
	Isopropanol	--	10.4	10.4	10.4	10.4	10.4	10.4	10.4
	Hair Styling	4.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6
	Polymer ¹								
	KOH (45% aqueous solution) ²	0.82	0.7	0.8	0.8	0.8	0.8	0.8	0.8
	DRO Water ³	17.4	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Potassium Chloride	0.02	0.05	0.02	-	-	-	-	-
	Potassium Acetate	-	-	-	-	0.09	-	-	-
	Magnesium Acetate	-	-	-	-	-	-	-	-
	Acetic Acid	-	-	-	0.06	-	-	-	0.06
	Fluorosurfactant ⁴	-	-	-	-	-	0.1	0.05	-
	AMP ⁵	-	-	-	-	-	-	-	-
		Example # (Weight Percent)							
		<u>IX</u>	<u>X</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>	<u>XVI</u>
	<u>Ingredient</u>								
	Ethanol, 200 proof	79.2	86.6	86.3	43.3	86.6	80.0	75.9	75.8
	Isopropanol	10.4	10.4	10.4	10.4	10.4	10.4	-	-
	Hair Styling	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
	Polymer ¹								
	KOH ²	0.8	-	-	-	-	-	3.3	3.3
	DRO Water ³	7.0	0.1	0.3	42.9	-	7.0	15.0	15.0
	Potassium Chloride	-	0.03	-	-	-	0.03	-	-
	Potassium Acetate	0.09	-	0.1	-	-	-	-	0.2
	Magnesium Acetate	-	-	-	-	-	-	0.1	-
	Acetic Acid	-	-	-	0.5	-	-	-	-

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Fluorosurfactant ⁴	-	-	-	-	0.05	-	-	-
AMP ⁵	-	0.3	0.3	0.3	0.3	-	-	-

- 5 ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone (PDMS) macromer - Example I, weight average molecular weight of about 150,000. Examples II-VI, weight average molecular weight of about 1.7 million; Examples VII-XIV, weight average molecular weight of about 800,000; Examples XV-XVI, weight average molecular weight of about 1.2 million.
- 10 ² Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors, except Examples XV and XVI, utilizing a 10% aqueous solution of potassium hydroxide.
- ³ Double reverse osmosis water.
- 15 ⁴ ZONYL FSK containing 47% fluorosurfactant conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2(CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and 53% Acetic Acid and minors, supplied by E.I. DuPont de Nemours & Co., Inc. (Wilmington, Delaware, USA).
- ⁵ 2-Amino-2-methyl-1-propanol.

20 The hair spray formulations are prepared by forming a premix of the polymer in isopropanol, and then adding the ethanol. For Examples I, XV and XVI, the polymer is added directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. If used, the neutralizing agent (KOH or AMP, or both) is

25 then added and mixed into the premix. Then, fluorosurfactant, any of the salts, and water, as may be applicable, are mixed into the composition.

 Adjuvants may also be added to the compositions, including, for example, perfume or fragrance. The hair spray compositions

30 prepared are especially suitable for pump spray application. The compositions will be characterized by good sprayability characteristics and hair styling performance

Example XVII

35 A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

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	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	78.5
	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
5	KOH (45%)	0.7
	DRO Water	7.0
	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.5

- 10 ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.
- ² FLUORAD FC-120 supplied by Minnesota Mining and Manufacturing Co. (3M), (St. Paul, Minnesota, USA) containing 25% ammonium perfluoroalkyl sulfonates, 37.5% ethanol and 37.5% water and minors.
- 15 Prepared as in Examples I-XVI.

Example XVIII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
20	Ethanol, 200 proof	89.1
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.7
	DRO Water	7.0
25	FLUORAD FC-120 ²	0.1
	ZONYL FSK	0.5

- ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.
- 30 Prepared as in Examples I-XVI.

Example XIX

A hair spray composition of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
35	Ethanol, 200 proof	78.8

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	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.8
	DRO Water	7.0
5	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.04

- ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 580,000.
 10 Prepared as in Examples I-XVI.

Examples XX-XXII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

		Example	Example	Example
		<u>XX</u>	<u>XXI</u>	<u>XXII</u>
15	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
	Ethanol, 200 proof	71.1	71.2	71.2
	Isopropanol	9.5	9.5	9.5
	Hair Styling Polymer ¹	2.4	2.4	2.4
20	KOH (45%)	0.6	0.6	0.6
	DRO Water	16.2	16.2	16.2
	ZONYL TBS ²	0.15	-	0.05
	ZONYL FSK	0.05	0.1	0.07

- 25 ¹ 60% t-butyl acrylate/20% acrylic acid/20% PDMS macromer, having a weight average molecular weight of about 800,000.
² ZONYL TBS, an anionic surfactant supplied by DuPont, containing 30-35% perfluoralkyl sulfonic acid ammonium salt, 2.4% acetic acid and 65%-70% water.
 30 Prepared as in Examples I-XVI.

Examples XXIII-XXV

		Example	Example	Example
		<u>XXIII</u>	<u>XXIV</u>	<u>XXV</u>
35	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
	Ethanol, 200 proof	78.9	79.4	78.2
	Isopropanol	10.4	10.4	11.2

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	Hair Styling Polymer ¹	2.6	2.6	2.8
	AMP	0.2	-	-
	KOH (45%)	0.6	0.4	0.5
	DRO Water	7.0	7.0	7.0
5	FLUORAD FC-120	0.1	0.1	0.2
	ZONYL FSK	0.05	0.05	0.09
	ZONYL TBS	0.07	-	-
	Fragrance	0.07	0.03	-

- 10 ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer, having a weight average molecular weight of about 860,000 (Example XXIII), and 1.5 million (Example XXIV); and 1.7 million (Example XXV).
Prepared as in Examples IX-XVI.

EXAMPLE XXVI

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A hair spray concentrate composition, of the present invention, which is suitable for aerosol dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
20	Ethanol, 200 proof	95.8
	Hair Styling Polymer ¹	3.0
	KOH	0.6
	AMP	0.4
	ZONYL FSK	0.25

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- ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer, having average molecular weight of about 690,000.

- ² ZONYL FSK supplied by DuPont, containing 40% mono- and bis-fluoroalkyl phosphates, ammonium salt, complexed with aliphatic quaternary methosulfate, 15% isopropyl alcohol and 40-45% water.

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Prepared as in Examples I-XVI. The concentrate is packaged in a conventional aerosol spray can and charged with a conventional liquifiable propellant at a propellant:concentrate weight ratio of 30:70.

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Examples XXVII-XXX

	<u>Ingredient (wt.%)</u>	<u>XXVII</u>	<u>XXVIII</u>	<u>XXIX</u>	<u>XXX</u>
	Ethanol, 200 proof	79.3	80.1	79.3	79.5
5	Isopropanol	10.4	10.4	10.4	10.4
	Hair Styling Polymer ¹	2.6	-	-	-
	Hair Styling Polymer ²	-	1.8	-	-
	Hair Styling Polymer ³	-	-	2.0	-
	Hair Styling Polymer ⁴	-	-	-	1.8
10	KOH (10% aqueous solution)	-	-	1.2	1.2
	HCl (10% aqueous solution)	0.6	0.6	-	-
	DRO Water	7.0	7.0	7.0	7.0
	Potassium Chloride	0.10	0.10	0.10	0.10
15	¹ 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/70% ethylmethacrylate, having a weight average molecular weight of about 1.2 million.				
20	² 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/60% ethylmethacrylate/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million.				
	³ 15% N,N dimethylacrylamide/70% isobutylmethacrylate/15% acrylic acid, having a weight average molecular weight of about 1.2 million.				
25	⁴ 15% N,N dimethylacrylamide/60% isobutylmethacrylate/15% acrylic acid/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million).				

Prepared as in Examples I-XVI, except for Examples XXVII and XXVIII, the HCl is added as the neutralizer.

30 The above compositions will exhibit good sprayability and when applied to the hair, provide good hair styling benefits.

In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, it can be desirable to purify the styling resin by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at

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25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, the resin can be purified by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

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CLAIMS:

1. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000;
 - (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof;
 - (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;
- said composition having a pH of 10 or less.

2. A liquid hair styling composition as in Claim 1, comprising from 0.1% to 15%, by weight, of said ionic hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle, and from 0.01% to 4%, by weight of said ionic strength modifier system.

3. A liquid hair styling composition as in Claim 1 or 2, wherein said ionic hair styling polymer comprises from 2% to 75% ionic monomers, and from 25% to 98% nonionic monomers.

4. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000; said ionic hair styling polymer comprising silicone-containing monomers, wherein when the composition is dried, the hair styling polymer separates into a discontinuous phase

which includes the silicone portion of said polymer and a continuous phase which includes the non-silicone portion;

- (b) a liquid vehicle selected from the group consisting of water, C₂-C₄ monohydric alcohols, and mixtures thereof;
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle; said composition having a pH of 10 or less.

5. A liquid hair styling composition as in Claim 4, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

6. A liquid hair styling composition as in Claim 4 or 5, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

7. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, or 6, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

8. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said ionic hair styling polymer has a weight average molecular weight of at least 500,000.

9. A liquid hair spray composition as in Claim 3 or 6, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl

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methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof, and said nonionic monomer is selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphamethylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof.

10. A liquid hairspray product comprising a hairspray composition and a spray dispenser means for containing and spraying said composition, said composition being contained in said spray dispenser means, said hairspray composition characterized in that it comprises:

- (a) an ionic, silicone macromer-containing hair styling polymer;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof,
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;

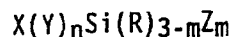
said composition having a pH of 10 or less and comprising from 10% to 90%, by weight, water, and from 10% to 80%, by weight, of said monohydric alcohols.

11. A liquid hairspray product as in Claim 10, comprising from 0.1% to 15%, by weight, of said hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle selected from the group consisting of C₂-C₄ monohydric alcohols and water, and from 0.01% to 4%, by weight, of said ionic strength modifier system.

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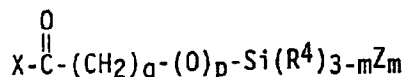
12. A liquid hairspray product as in Claim 10 or 11, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

13. A liquid hair styling composition or product as in Claim 4, 5, 6, 10, 11, or 12, wherein said silicone macromer-containing monomers have the formula:



wherein X is a vinyl group; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500; n is 0 or 1; and m is an integer from 1 to 3.

14. A liquid hair spray composition or product as in Claim 13, wherein said silicone macromer-containing monomer is:

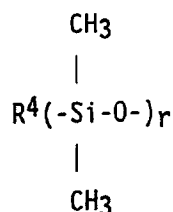


wherein m is 1, 2, or 3, p is 0 or 1, q is an integer from 2 to 6,

X is CH=C-



R¹ is -H or -COOH, R² is -H, -CH₃, or CH₂COOH, R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl, and Z is



wherein r is an integer from 5 to 700.

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15. A liquid hair spray product as in any of Claims 10-14, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

16. A liquid hair spray product as in any of Claims 10-15, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

17. A liquid hair spray composition or product as in Claim 16, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof.

18. A liquid hair spray composition or product as in Claim 17, wherein said polymer comprises 15% to 80% of said ionic monomer, 50% to 90% of nonionic monomer selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphas-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof and 2% to 25% of said silicone-containing monomer.

19. A method for providing hair setting benefits to the hair, comprising spraying an effective amount of any of the compositions of Claims 1-18 to hair.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/06975

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61K7/06; A61K7/11		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^a	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 412 704 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 cited in the application see the whole document ---	1-19
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<p>^a Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18 DECEMBER 1992		30.12.92
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		GAC G.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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SA 64051**

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ИПО ТОРМ 20679

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US93/04429 (22) International Filing Date: 11 May 1993 (11.05.93) (30) Priority data: 07/883,974 15 May 1992 (15.05.92) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: TORGERSON, Peter, Marte ; 4127 U.S. Rt. 35 NW, Washington Ct. House, OH 43160 (US). BALCHUNAS, Anthony, Thomas ; 5468 Yosemite Drive, Fairfield, OH 45014 (US).	(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US). (81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(54) Title: ADHESIVE AGENT CONTAINING POLYSILOXANE-GRAFTED POLYMER, AND COSMETIC COMPOSITIONS THEREOF (57) Abstract Polymeric adhesive agents are disclosed which comprise polysiloxane grafted polymers wherein: (a) the polymers are made by polymerization of polysiloxane-containing monomers and non-polysiloxane-containing monomers, typically by free radical polymerization; (b) the adhesive agent has a weight average molecular weight of at least about 20,000 and contains from about 1 % to about 50 %, by weight, of polysiloxane-containing monomer; and (c) the weight percentage of silicon present as unreacted polysiloxane-containing monomer and silicone-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes based on the total silicon present as unreacted silicon monomer and polysiloxane-grafted polymer is about 15 % or less. Also, the adhesive agent contains no more than about 4 %, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes. Cosmetic compositions containing such adhesive agents are also disclosed.		

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ADHESIVE AGENT CONTAINING
POLYSILOXANE-GRAFTED POLYMER, AND
COSMETIC COMPOSITIONS THEREOF

5

TECHNICAL FIELD

The present invention relates to adhesive agents containing polysiloxane-grafted polymers and to compositions, such as cosmetic compositions, containing such adhesive agents. This invention especially relates to adhesive agents useful for hair setting purposes, and to hair setting compositions containing such adhesive agents.

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has recently been discovered that hair care compositions containing polysiloxane-grafted polymers can provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays,

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tonics, lotions, gels, and mousses. The compositions can provide these benefits to hair without leaving the hair stiff or sticky/tacky feel, as do conventional hair setting ingredients.

5 These types of adhesive, film-forming, polysiloxane-grafted polymers can also be used for other purposes, such as topical application to skin for cosmetic purposes or as a means for delivery of medicaments. The film forming agents can also be used in a wide variety of other adhesive areas, e.g. adhesive paper or binding materials, etc.

10 Polysiloxane-grafted polymers are disclosed for use in EPO Application 90307528.1, published January 16, 1991 as EPO Publication 0 408 311 A2, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, 15 Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991. Adhesive 20 compositions containing film-forming polysiloxane-grafted polymers are also disclosed in U.S. Patent 4,728,571, issued March 1, 1988, Clemens et al., U.S. Patent 5,021,477, issued June 4, 1991, Garbe et al., U.S. Patent 4,981,902, issued January 1, 1991, Garbe et al., U.S. Patent 4,988,506, issued January 29, 1991, Mitra et al., 25 and U.S. Patent 4,981,903, Mitra et al., issued January 1, 1991, Mitra et al.

30 Whereas excellent performance can be obtained with these polysiloxane-grafted polymers, particularly for hair setting compositions, it remains desirable to achieve improved adhesive performance. It also remains desirable to achieve higher levels of tactile softness for a given level of adhesion for compositions containing these adhesive agents. In particular, for example, it is desirable to provide hair setting compositions with improved hold and/or higher tactile softness for a given level of hold. It

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is an object of this invention to provide adhesive agents that can provide such enhanced levels of performance.

These and other benefits will become readily apparent from the detailed description which follows.

5 Unless otherwise indicated, all percentages and ratios herein are by weight. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

SUMMARY OF THE INVENTION

10 The present invention relates to a polymeric adhesive agent, especially a film-forming agent, comprising a polysiloxane-grafted polymer made by the polymerization of polymerizable, polysiloxane containing monomers with polymerizable non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average
15 molecular weight of at least about 20,000, contains from about 1% to about 50%, by weight, of the polysiloxane-containing monomer, and the weight percentage of silicon present as unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes
20 based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below about 10,000,000.
25

In another embodiment, the present invention provides cosmetic compositions, especially hair care compositions, eg. hair setting compositions, comprising the adhesive agent hereof and a carrier suitable for application to the hair.

DETAILED DESCRIPTION OF THE INVENTION

30 The essential, as well as various optional, components of the present invention are described below.

Polymeric Adhesive Agent

The polymeric adhesive agent hereof comprises a film-forming
35 polysiloxane-grafted polymer, made by the polymerization of

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polysiloxane-containing monomers with non-polysiloxane-containing monomers such that said adhesive agent has a weight average molecular weight of at least about 20,000, comprises from about 1% to about 50%, by weight, of the polysiloxane-containing monomers, and the weight percentage of unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes: to total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less, more preferably about 5% or less. The level of polysiloxane-containing monomers in the adhesive agent, for purposes hereof, includes monomer present in either unreacted (eg., unpolymerized) form as well as monomer incorporated into the adhesive agent in polymer form. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below about 10,000,000, preferably less than about 3% more preferably less than about 2%, most preferably less than about 1%. The limitation pertaining to the adhesive agent sets forth the maximum viscosity level, as described above, can also be limited to is preferably about 1,000,000, about 100,000 or about 10,000, etc.

Cosmetic compositions of the present invention typically contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of the adhesive agent, although higher or lower amounts may be used for particular applications. The adhesive agent hereof can also be used to advantage in other cosmetic products, such as make-up; mascara and eye-liner, nail polish, etc., as well as topical skin products such as creams and lotions, including for delivery of medicaments or other ingredients to the skin. The adhesive agent hereof can further be used for other adhesive applications, such as adhesive paper and backing paper, etc.

The adhesive agent should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the

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invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, especially for cosmetic compositions, the adhesive agents hereof when dried to form a film have a Tg of at least about -20°C, preferably at least about 20°C, so that they are not sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer. Preferably, the Tm, if any, is also above about -20°C, more preferably above about 20°C.

The polymers useful in the compositions of the present invention are polysiloxane-grafted polymers of polymerizable "silicone-containing", or "polysiloxane-containing", monomers with non-silicone-containing monomers. The polysiloxane-grafted polymers should satisfy the following four criteria:

- (1) when dried the polymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently grafted to the non-silicone portion; and
- (3) the molecular weight of the silicone portion is at least about 500; and

When used in a composition, such as a cosmetic composition for application to the hair or skin, the non-silicone portion should render the entire polymer soluble or dispersible in the composition vehicle and permit the polymer to deposit on the intended surface, eg. hair or skin.

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The most preferred polymers comprise an organic backbone, especially a carbon backbone such as a vinyl polymeric backbone, and also preferably, a polydimethylsiloxane macromer having a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000, is grafted to the backbone. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers. These include vinyl monomers, and other condensation monomers (eg., those that polymerize to form polyamides and polyesters) and ring-opening monomers (eg., ethyl oxazoline and caprolactone). The polymer is such that when it is formulated into the finished composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer which results in the desired combination of tactile feel and setting, film-forming, or adhesive benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the

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concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These polymers are comprised of: at least one free radically polymerizable vinyl monomer or monomers (A); and optionally at least one reinforcing monomer copolymerizable with A which is more hydrophilic than A and is selected from the group consisting of hydrophilic monomers and macromers having a Tg or a Tm above about -20°C (B). The polymers also comprise polysiloxane-containing monomers. (C) Polymerizable macromers which can be used herein shall be referred to herein collectively with polymerizable monomers as "monomers", for convenience. Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers means monomers which do not form substantially water insoluble homopolymers. Suitable polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed

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August 27, 1991, all of which are incorporated by reference herein.

5 The polysiloxane-grafted polymers hereof comprise from about 1% to about 50%, by weight of C monomers, i.e., the polysiloxane-containing monomers, and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers, which can be monomers selected from the group consisting of A and B monomers, and mixtures thereof.

10 Representative examples of hydrophobic, A monomers are acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 15 t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include 25 n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, A is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

30 Representative examples of hydrophilic, B monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, 35 diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers

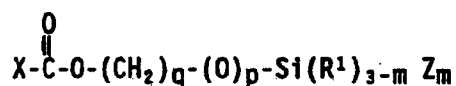
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(such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

The preferred polymerizable polysiloxane-containing monomer (C monomer) can be exemplified by the general formula:



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:



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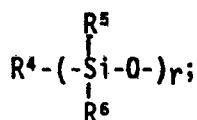
In this structure, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R⁴ is alkyl); X is

30



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is

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5 R^4 , R^5 , and R^6 independently are lower alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen or hydroxyl (preferably R^4 , R^5 , and R^6 are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R^4 , R^5 , and R^6 are methyl, $p=0$, and $q=3$.

10 In general, the total of A and B monomers in the adhesive agent polymer will preferably be from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95)%, by weight of the polymer of the adhesive agent. The level of A monomers can be from 0% to about 99%; the level of B monomers, from 0% to about 99%; and the level of C monomers, from 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of monomer C. The
15 composition of any particular adhesive agent polymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the adhesive agent polymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous
20 formulation or other polar or hydrophilic solvents preferably have from about 0% to about 85% (preferably from about 5% to about 70%) monomer A, from about 14% to about 95% (preferably from about 29% to about 80%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers which
25 are dispersible in aqueous formulations have the preferred composition: from about 0% to about 70% (preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers
30 which are soluble or dispersible in less polar or nonpolar solvents, such as cyclomethicone, preferably comprise from about 5% to about 98% (preferably from about 50% to about 90%) of monomer A, from 0 to about 80% (preferably from 0% to about 45%, most preferably from 0% to about 20% of monomer B, and from about

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1% to about 40% (preferably from about 2% to about 25%) of monomer C.

5 The polysiloxane-grafted polymers can be synthesized as follows. In general, the polymers can be made by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The
10 filming forming, cosmetic agent comprising this product is prepared by substantially removing the unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers which have a fluid viscosity at 25°C of below about 10,000,000, to the levels defined by silicon present as described above. The monomer and polymeric material removed are both of relatively low molecular weight, compared to the molecular weight of the cosmetic agent hereof.

15 It is not intended to necessarily exclude from this invention any polysiloxane-grafted polymer made by free radical polymerization or by means other than free radical polymerization, so long as the product is substantially free of the above-mentioned, undesired materials, either by means of
20 purification subsequent to reaction or as a result of an improved reaction or different type of synthesis. However, it is to be understood that block copolymers of alternating organic block and silicone blocks are not included as polysiloxane-grafted polymers.

25 The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable.
30 Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur,
35 assuming thermal initiators are used. Alternatively, redox or

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radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 20 parts acrylic acid, 60 parts t-butylacrylate, and 20 parts polysiloxane (10,000 MW)-containing monomer in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven. A similar procedure can be used to make an 80%/120% t-butyl acrylate/polysiloxane (10,000 MW)-containing monomer. Ethyl acetate is the preferred solvent for this synthesis.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C in a water bath. Add

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initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62°C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

10 Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts isobutyl methacrylate, 3.5 parts 2-ethylhexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

25 Removal of unwanted polysiloxane-containing monomer and/or polysiloxane-grafted polymeric material that has viscosity below 10,000,000 at 25°C from free radically polymerized product can be done by any means known in the art. The materials to be removed, in general, will be of lower molecular weight than the average molecular weight of the polymer material prior to extraction. Also, such materials to be removed will contain a relatively high proportion of polysiloxane relative to the organic component-generally, although not necessarily, in excess of 50% polysiloxane.

30 Techniques suitable for removing the unwanted material include a variety of standard procedures known in the art.

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One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide.

5 Supercritical fluid extraction is carried out on polymer which has been dried from the original reaction mixture to remove excess reaction solvent. Dried polymer is preferably ground to create a fine powder, which allows for increased surface area and maximum extraction efficiency. Extraction can be carried out using supercritical carbon dioxide in conventional extractors suitable for supercritical fluid extraction. The extraction
10 should be conducted at a temperature of at least about 40 deg C and a pressure of between about 400-600 atmospheres. The particular temperature and pressure will depend upon criteria well known in the art, such as specific solvent, polymer sample size, fineness of the ground material, and the desired extraction efficiency. Extraction occurs via continuous purging under
15 pressure with supercritical carbon dioxide, typically over a period of about 1-4 hours. Unreacted polysiloxane-containing monomer and low molecular weight polysiloxane-containing polymer is solubilized by carbon dioxide and is then transported away from the remaining polymer via standard procedures, e.g., by a transfer
20 line.

Another generally applicable method is membrane separation, performed in accordance with standard techniques known in the art.

25 A method which can be useful, particularly for adhesive agents utilizing polysiloxane-grafted polymers that are soluble in water, alcohol, or other polar solvents, is solvent extraction with a nonpolar solvent. Suitable solvents include C₃-C₈ hydrocarbons, preferably C₅ -C₆ hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is
30 precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average T_g of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The temperature should be high enough so that the polymer softens, but
35 not so high such that it congeals. The T_g of the polymer will

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vary from species to species of polymer. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will depend upon the reflux temperature of the solvent; the T_g of the polysiloxane-grafted polymer of the adhesive agent, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and the polysiloxane-containing polymer having viscosity at 25°C below about 10,000,000, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours, more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

Analysis of the polymer reaction product and the extracted materials, and the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resonance (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, and atomic absorption and emission spectroscopies.

Carrier

The cosmetic compositions of the invention comprise the a carrier, or a mixture of such carriers, which are suitable for application to skin or hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%; most preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular polymer

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to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

5 The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone-grafted polymer being used. The
10 silicone-grafted polymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (e.g. C₁-C₆ monohydric alcohols, such as ethanol and isopropanol), hydro-
15 alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), lin-
alool, hydrocarbon esters (such as ethyl acetate, dibutyl phtha-
late), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-
tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl
20 pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl
cyclopentasiloxane, cyclomethicone, and dimethicone (having for
example, viscosity at 25°C of about 15 centipoise or less), and
mixtures thereof. Preferred solvents include water, ethanol,
volatile silicone derivatives, and mixtures thereof. The solvents
25 used in such mixtures may be miscible or immiscible with each
other.

Where the cosmetic compositions are conditioner compositions, such as hair rinses or skin conditioners the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant
30 vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science
35 82-91 (1968); Barry, et al., "The Self-Bodying Action of

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Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The carrier may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle

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material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred carrier for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al., and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference.

Carriers, suitable for use with the present invention include, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are especially preferred, particularly if the product is a hair spray composition and most especially if it is a spray composition having relatively low levels of volatile organic solvents, such as alcohols, and relatively high levels of water (e.g., in excess of about 10%, by weight water). If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

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Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or can having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStegge, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Optional Ingredients

The cosmetic compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials typically have the respective formulae ROS_3M and

- 20 -

$RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine.

5 Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



10 wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18
15 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

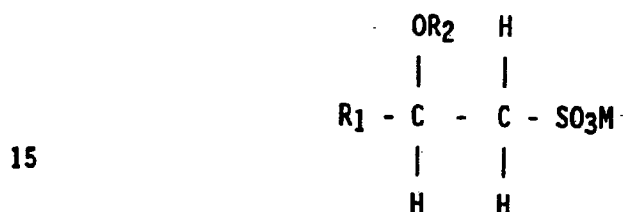
20 Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for
25 example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

30 Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

35 Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The

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term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides such as those corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional representation of a semipolar bond).

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

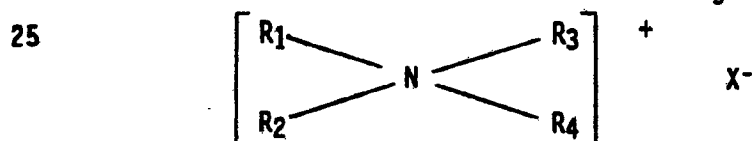
6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

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Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9,-trioctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 - R_4 are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino

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groups. The longer chain aliphatic groups, eg., those of about 12 carbons, or higher, can be saturated or unsaturated.

Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

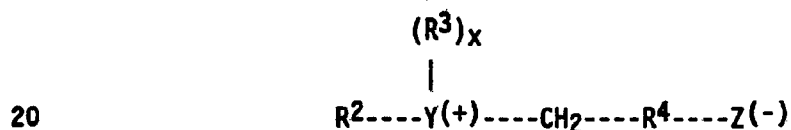
Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R_1 and R_2 have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable

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amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl

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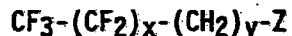
bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by
5 coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $RCONH(CH_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this
10 invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched
15 chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-
20 propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.
25

Fluorosurfactant

The compositions of the present invention can contain, fluorosurfactant. Suitable fluorosurfactant can be cationic, anionic, amphoteric, zwitterionic, nonionic or a mixture thereof.

30 Fluorosurfactants include perfluorinated compounds such as those represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to
35 17, particularly from 7 to 11, and y is an integer from 0 to 4,

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and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Cationic fluorosurfactants include fluorinated alkyl quaternary ammonium salts having a variety of anionic counterions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably an iodide; and those fluorosurfactants conforming to the formula $R_fCH_2CH_2SCH_2CH_2N^+(CH_3)_3[CH_3SO_4]^-$ wherein $R_f = F(CF_2CF_2)_{3-8}$, such as Zonyl FSC® supplied by DuPont. Preferred fluorinated alkyl quaternary ammonium iodides are supplied under the tradename Fluorad FC-135® supplied by 3M.

Anionic fluorosurfactants include mono-, and bis-perfluoroalkyl phosphates, such as Zonyl FSP® supplied by DuPont and conforming to the general formulae $(R_fCH_2CH_2O)P(O)(ONH_4)_2$ $(R_fCH_2CH_2O)_2P(O)(ONH_4)$ wherein $R_f = F(CF_2CF_2)_{3-8}$; mono- and bis-fluoroalkyl phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as Zonyl FSJ® supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as Zonyl TBS® supplied by DuPont and conforming to the formula $R_fCH_2CH_2SO_3X$ wherein $R_f = F(CF_2CF_2)_{3-8}$ and $X = H$ and NH_4 ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as Zonyl RP® supplied by DuPont; amine

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perfluoroalkyl sulfonates, such as Fluorad FC-99® supplied by 3M; ammonium perfluoroalkyl sulfonates, such as Fluorad FC-93®, Fluorad FC-120® and L-12402®, supplied by 3M; potassium perfluoroalkyl sulfonates, such as Fluorad FC-95® and Fluorad FC-98® supplied by 3M; potassium fluorinated alkyl carboxylates, such as Fluorad FC-129® supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143® supplied by 3M; and those fluorosurfactants conforming to the general formula $R_fCH_2CH_2SCH_2CH_2CO_2Li$ wherein $R_f=F(CF_2CF_2)_{3-8}$, such as Zonyl FSA® supplied by DuPont.

Amphoteric fluorosurfactants include fluorinated alkyl amphoterics such as Fluorad FC-100® supplied by 3M.

Zwitterionic fluorosurfactants preferred for use in the present compositions are those fluorosurfactants conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ such as Zonyl FSK® supplied by DuPont.

Fluorosurfactants can be used alone or in combination in the hair spray compositions of the present invention.

Fluorosurfactants, when used, will typically be present at from about 0.01% to about 2%, preferably from about 0.01% to about 1.5%, by weight of the composition.

The above-mentioned surfactants can be used alone or in combination in the compositions hereof.

The cosmetic compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium

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sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as
5 any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin, disobutyl adipate,
10 butyl stearate, and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions generally will be between
15 about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The cosmetic compositions of the present invention can be
20 made using conventional formulation and mixing techniques. Methods of making various types of cosmetic compositions are described more specifically in the following examples.

Method of Use

The cosmetic compositions of the present invention are used
25 in conventional ways to provide the conditioning/styling/hold/adhesive/film-forming or other benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair or skin, which may
30 then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, skin lotion, film-forming skin lotion with medicament, and tonic products). By "effective amount" is meant an amount sufficient to provide the film-forming
35 benefits desired. Preferably, hair rinse, mousse, and gel

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products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetics and skin lotions are applied to face, skin, or eye area in the conventional manners of usage for those types of products.

In another aspect hereof, adhesive agents containing polysiloxane-grafted polymers, such as those described in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987 and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, can be used in adhesive products such as adhesive tapes and backing sheets for adhesive materials. Thus, the adhesive agents hereof also can include non-pressure sensitive as well as pressure sensitive film-forming polymers.

The following experimentals and examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

Experimental A

A 60%/20%/20% t-butyl acrylate/acrylic acid/polydimethylsiloxane-containing (PDMS) vinyl monomer (10,000 MW) is made by free radical polymerization in an acetone reaction medium, as described above for Polymer I. The percentages represent the weight percent of the total monomer added to the reaction.

The reaction product is precipitated out of the acetone by water addition and dried. Hexane extraction of the reaction product is then performed by adding an excess of hexane to the reaction product and heating to reflux, about 70°C. The Tg of the non-silicone portion of the adhesive agent polymer is about 63°C. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are conducted

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in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Experimental B

5 An 80%/20% t-butyl acrylate PDMS (10,000 MW) polymer is made according to the same procedures as for Polymer I, above, except that the monomers that are polymerized are 80%, by weight, t-butyl acrylate and 20%, by weight, of the PDMS-containing vinyl monomer. The reaction medium is ethyl acetate.

10 The reaction product is precipitated out of the reaction solvent by water addition and dried. The polymer is next ground to a fine powder in preparation for supercritical fluid extraction with carbon dioxide. The extraction is carried out at a temperature of about 40°C and a pressure of about 600 atmospheres. 15 The extraction vessel is continuously purged under pressure with supercritical carbon dioxide over a period of about 1 hour.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

25 EXAMPLES I-III

The following are hair spray compositions representative of the present invention.

<u>Component</u>		<u>Example # (Weight %)</u>		
		<u>I</u>	<u>II</u>	<u>III</u>
30	Polysiloxane-Grafted Polymer (Exp. A)	4.5	4.5	4.5
	Ethanol	79.0	79.0	86.4
	Diisobutyl adipate	0.7	--	--
	Potassium Hydroxide Solution (45% conc)	1.0	1.0	1.0
	Perfume	0.2	0.2	0.2
	FC-120 Fluorosurfactant (3M Co)(25% active)	--	--	0.14
	Water	q.s. to 100%		

35 This product is prepared by dissolving the silicone polymer to the ethanol and mixing for several hours until all the polymer

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is dissolved. Plasticizer is then added, if applicable. Potassium hydroxide is then added. Water or water/surfactant, as applicable, is added. Fragrance is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

EXAMPLE IV

The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Polysiloxane-Grafted Polymer (Exp. A)	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

EXAMPLE V

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Polysiloxane-Grafted Polymer (Exp. A)	2.00
Ethanol	10.00
PEG 150 distearate	2.00
NaOH	0.15
Glydant ¹	0.38
Perfume	1.00
DRO H ₂ O	q.s.

¹ preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient

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temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE VI

5 The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Thioglycolic acid	5.00
	Monoethanolamine	6.00
	Polysiloxane-Grafted Polymer (Exp. A)	1.50
10	PEG 10 monostearate	0.50
	DRO H ₂ O	q.s.

The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60°C and then cooling to ambient temperature.

15

EXAMPLE VII

The following is a styling gel composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	2.00
20	Carbopol 940 ¹	0.75
	Triethanolamine	1.00
	Dye solution	0.05
	Perfume	0.10
	Laureth-23	0.10
25	DRO H ₂ O	q.s.

¹ cross-linked polyacrylic acid, commercially available from B. F. Goodrich

This batch is made by mixing the listed components together in a conventional manner.

30

EXAMPLE VIII

The following is a hair mousse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	3.00
35	Ethanol	15.00

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	Cocamine oxide	0.60
	D.C. 190 ¹	0.20
	Cocamide DEA	0.30
	Perfume	0.10
5	Isobutane	7.00
	DRO H ₂ O	q.s.

¹ dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

Examples IX-X

The following are hair styling/conditioning rinse compositions representative of the present invention.

	<u>Composition</u>	<u>IX</u>	<u>X</u>
	Citric Acid	0.02	0.02
	Sodium Citrate	0.09	0.09
	Cetyl Alcohol	0.12	0.12
20	Stearyl Alcohol	0.08	0.08
	Natrosol Plus CS Grade D-67 ¹	1.05	1.10
	Xanthan Gum ²	0.25	0.25
	Styling Polymer Premix		
	Polysiloxane-Grafted Polymer (Exp. B)	1.75	1.75
25	Octamethyl cyclotetrasiloxane	5.98	5.98
	Decamethyl cyclopentasiloxane	2.56	2.56
	Butyl Stearate	0.15	0.15
	Kathon CG	0.03	0.03
	Perfume	0.33	0.33
30	Conditioner Premix		
	DRO Water	12.18	11.88
	Adogen 442-100P ⁴	0.75	0.75
	Adogen 471 ⁵	--	0.60
	Stearyl Trimethyl		
35	Ammonium Chloride	0.30	--

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Silicone Gum Premix

	Decamethyl cyclopentasiloxane	1.42	1.42
	Polydimethyl Siloxane Gum ³	0.25	0.25
	Amodimethicone (Dow Corning Q2-8220)	--	0.10
5	DRO Water	q.s.	q.s.

¹Hydrophobically modified hydroxyethyl cellulose from Aqualon Corp.

²Readily dispersible xanthan gum

10 ³SE-76 gum available From General Electric

⁴Ditallow dimethyl ammonium chloride, Sherex Chemical Co., Dublin, Ohio, USA.

⁵Tallow trimethyl ammonium chloride, Sherex Chemical Co.

15 The styling polymer premix is prepared by combining the polymer, the octamethyl tetrasiloxane and decamethyl pentasiloxane, and butyl stearate.

The silicone gum premix is prepared by combining and mixing (in a separate vessel) the silicone gum and decamethyl cyclopentasiloxane until homogeneous.

20 The conditioner premix is prepared by combining and mixing (in a separate vessel) DRO water, any primary and secondary thickeners (premelted if necessary to ensure homogeneity) at 82° the silicone gum premix, and amodimethicone at 71°C, until homogeneous.

25 In another vessel, the DRO water is heated to 71°C. Citric acid, sodium citrate, cetyl alcohol, stearyl alcohol and Natrosol Plus CS grade D-67 are added and mixed until homogeneous. The xanthan gum is added and mixed until homogeneous. The styling polymer premix, Kathon CG and perfume are added and mixed until
30 homogeneous. The composition is further dispersed with an in-line homogenizer (such as Tekmar homogenizer) and then cooled to 38°C.

35 The conditioner premix is also further dispersed with an in-line homogenizer and cooled to 38°C and added to the final vessel, mixing until homogeneous to form the styling rinse composition.

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When the compositions defined in Examples I-X are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

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EXAMPLE XI

An aerosol hair spray composition of the present invention is prepared as follows:

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted	4.00
10	Polymer (Exp. A)	
	Water	11.00
	Ethanol	63.50
	KOH (45% solution)	0.90
	Isobutane	15.00
15	Diffuoroethane	6.00

All of the ingredients except for the propellants are mixed together at ambient temperature until the polymer is dissolved. The mixture is placed in an aerosol can which is then equipped with a conventional aerosol spray can valve, which is vacuum crimped in place. The propellants are then filled through the valve and the can is equipped with a conventional aerosol spray can activator.

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WHAT IS CLAIMED IS:

1. A polymeric adhesive agent comprising a polysiloxane-grafted polymer, made by the polymerization of polysiloxane-containing monomers with non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average molecular weight of at least 20,000 and contains from 1% to 50%, by weight, of polysiloxane-containing monomers, characterized in that said adhesive agent: has a weight percentage of silicon present as unreacted polysiloxane-containing monomer and polysiloxane grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer of 15% or less; and contains no more than 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

2. An adhesive agent as in Claim 1, wherein the weight percentage of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymers having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is 10% or less, preferably 5% or less, and said adhesive agent contains no more than 3%, preferably no more than 1%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

3. An adhesive agent as in Claim 1 or 2, wherein said weight average molecular weight of said adhesive agent is at least 75,000, preferably at least 100,000, more preferably from 100,000 to 750,000.

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4. An adhesive agent as in Claim 1, 2, or 3, wherein said polymer comprises from 50% to 99%, by weight of the adhesive agent, of polymerizable, ethylenically unsaturated polymerizable monomers, and from 1% to 50% preferably from 2% to 25% of polysiloxane-containing monomers having a molecular weight of at least 1,000 and the general formula:

$$X(Y)_nSi(R)_{3-m}(Z)_m$$

wherein

X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, hydroxyl, lower alkyl, aryl, alkaryl, alkylamino, or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

n is 0 or 1, and

m is an integer from 1 to 3.

5. An adhesive agent as in Claim 4, wherein said non-polysiloxane-containing monomer is a free radically polymerizable vinyl .

6. An adhesive agent as in Claim 4 or 5, wherein said non-polysiloxane-containing monomers are selected from the group consisting of hydrophobic monomers selected from the group consisting of acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide,

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N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof, and hydrophilic monomers selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, salts of the above acids and amines, and mixtures thereof.

7. An adhesive agent as in Claim 6, wherein said hydrophobic monomers are selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

8. An adhesive agent as in Claim 6 or 7, wherein said hydrophilic monomers are selected from the group consisting of acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of the above acids and amines, and mixtures thereof.

9. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 85%, by weight, of said hydrophobic monomers, from 14% to 95% of said hydrophilic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 29% to 80% of said

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hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

10. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 70%, by weight, of said hydrophobic monomers, from 20% to 80% of said hydrophilic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 20% to 60% of said hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

11. A hair care composition useful for styling hair, comprising the adhesive agent of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 and a carrier suitable for application to the hair.

12. A hair care composition as in Claim 11, in the form of liquid suitable for spray application to the hair, wherein said carrier comprises water, C₁-C₆ monohydric alcohol, or a mixture thereof.

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(21) International Application Number: PCT/US94/05245 (22) International Filing Date: 11 May 1994 (11.05.94) (30) Priority Data: 9312618.3 18 June 1993 (18.06.93) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): WELCH, Rosemary, Jane [GB/GB]; 15 Thorncroft Englefield Green, Surrey TW20 0SB (GB). DODSWORTH, Emma, Louise [GB/GB]; Stylehurst Cottage, Wear Street, Capel, Surrey RH5 5JD (GB). CHAMBERS, Gillian [GB/GB]; Flat 5, 6 Avenue Road, Staines, Middlesex TW18 3AW (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIR COSMETIC COMPOSITIONS (57) Abstract A liquid hair cosmetic composition comprising: (a) from about 0.1 % by weight to about 10 % by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000; (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15 % of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25 % to about 80 % of the acid groups on the silicone-containing copolymer; and (c) from 0 % to about 10 % by weight of water; and (d) the balance comprising a carrier suitable for application to hair. The liquid hair cosmetic products have an improved clarity and demonstrate excellent hair styling benefits in addition to hair feel attributes and ease of brush out.		

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HAIR COSMETIC COMPOSITIONS

Technical Field

The present invention relates to hair cosmetic compositions. More particularly, this invention relates to liquid hair cosmetic compositions containing silicone grafted hair styling polymer neutralised with a mixture of inorganic and organic neutralising agents and having improved product stability and style retention properties.

Background Of The Invention

The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style retention is typically achieved by the use of resins, such as AMPHOMER, supplied by

National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hairspray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000. When such resins are incorporated into pump and aerosol hairsprays, they can provide suitable style retention attributes. However, such resins are found to be deficient in the area of hair feel and can give a stiff hair feel.

Recently, it has been found that certain neutralisable polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins without the tacky hair feel traditionally associated with non-silicone hair fixative polymers. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EP-A-0,408,311 A2 issued January 11th 1991, Hayama, et al., US-A-5,061,481, issued October 29th 1991, Suzuki et al., US-A-5,106,609, Bolich et al., issued April 21st 1992, US-A-5,100,658, Bolich et al., issued March 31st 1992, US-A-5,100,657, Ansher-Jackson, et al., issued March 31st 1992 and US-A-5,104,646, Bolich et al., issued April 14th 1992.

It is well known that at least partial neutralisation of the silicone macromer containing hair styling polymer is necessary to maximise its utility in hair styling compositions. Typically, silicone grafted copolymers neutralised with an inorganic neutraliser exhibit good solubility in hairspray compositions containing 15% water. However, it has now been found that such inorganic neutralised systems are less soluble in compositions which contain lower levels of water and lead to hazy, colloidal systems. It has also been found that by using selected mixtures of inorganic and organic neutralisers in liquid hair cosmetic compositions, systems of excellent clarity can be achieved.

Thus a need exists for hair styling compositions which have a clear appearance, deliver effective style retention, impart a hair conditioning effect, have a non-sticky hair feel, are easily brushed out and at the same

time have stable product and viscosity characteristics and remain fully stable under long term and stressed temperature storage.

Summary of the Invention

According to one aspect of the invention, there is provided a liquid hair cosmetic composition comprising:-

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% of the acid groups on the silicone-containing copolymer;
- (c) from 0% to about 10% by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

The preferred neutralising systems for use herein comprise a combination of organic and inorganic base. From about 30% to about 95% more preferably from about 55% to about 75%, most preferably from about 60% to about 70% of the acidic groups of the polymer should be neutralised with the chosen mixed neutralising system, the level of neutralisation being determined in the manner described herein below.

The essential, as well as the optional, components of the present invention are described below. All levels and ratios are on a weight basis unless otherwise specified.

Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1 % to about 10.0%, preferably from about 0.5% to about 8.0% and especially from about 1 % to about 6% of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers preferably have a weight average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000, most preferably from about 90,000 to about 300,000 and, preferably, have a Tg of at least about -20°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

The molecular weights and molecular weight distributions of the polymers utilised in the compositions according to the present invention are determined by Size Exclusion Chromatography (SEC). In practise, polymers comprise a distribution of molecular weight species that gives rise to their unique properties. Separation of the molecules is accomplished by Size Exclusion Chromatography (SEC) using a crosslinked polystyrene -divinylbenzene column (MW range = 100 - 10⁷) with a differential refractive index detector and a differential viscometer. A universal calibration curve is prepared from monodispersed polystyrene standards of known molecular weight (MW) and molecular weight distribution (MWD). MW and MWD of the given polymer are determined based on concentration and viscosity responses relative to the calibration.

Preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg above about -20°C and, grafted to the backbone, a silicone containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a

discontinuous phase which includes the silicone containing macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits.

In its broadest aspect, the copolymers utilized in the present application comprise a silicone-containing monomer (hereafter identified as C) together with a hydrophilic carboxylate-containing monomer (B) and optionally a lipophilic monomer (A).

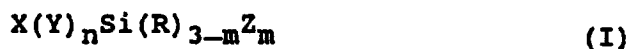
Examples of useful copolymers and their preparation are described in detail in US-A-4,693,935, Mazurek, issued September 15th 1987, and US-A-4,728,571, Clemens et al., issued March 1st 1988. These copolymers comprise monomers A, B and C as defined above. In preferred embodiments, A comprises at least one free radically polymerizable vinyl monomer or monomers and B comprises at least one reinforcing monomer copolymerizable with A and selected from the group consisting of carboxylate-containing monomers and macromers having a T_g or a T_m above about -20°C . B can be up to about 98%, preferably up to about 80%, more preferably up to about 30%, of the total monomers in the copolymer. Monomer C comprises from about 0.1% to about 50.0% of the total monomers in the copolymer.

Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol (2-methyl-1-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene;

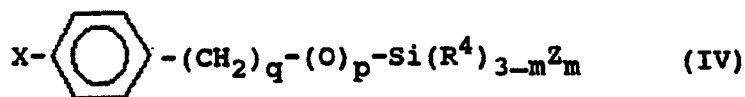
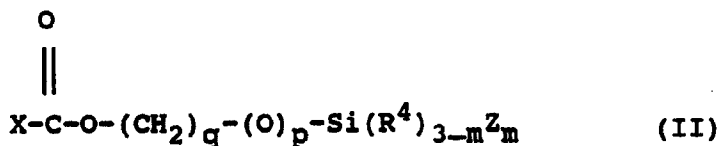
cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

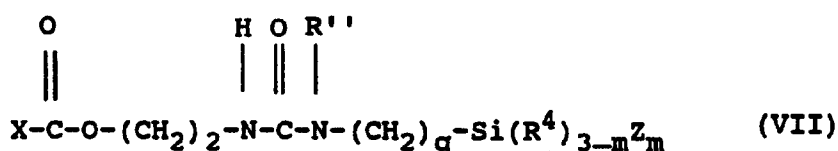
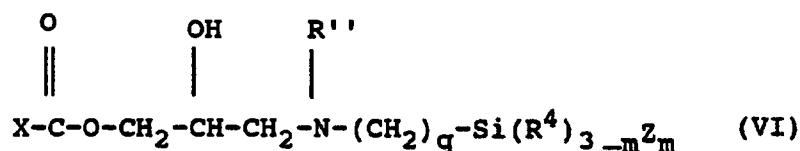
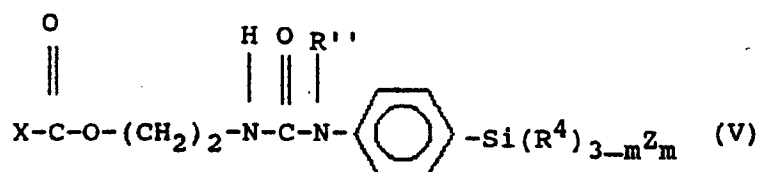
Representative examples of B (hydrophilic) neutralisable monomers containing a carboxyl moiety include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, and itaconic acid. Preferred B monomers include acrylic acid and methacrylic acid and mixtures thereof.

The C monomer preferably has the general formula (I):



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is hydrogen, C₁-C₄ alkyl, aryl, alkyl amino, tri(C₁-C₄ alkyl)siloxy or C₁-C₄ alkoxy; Z is a monovalent siloxane polymeric moiety; n is 0 or 1; and m is an integer from 1 to 3. C has a number average molecular weight of, at least 500, preferably from 1,000 to 50,000. Preferably, the C monomer is selected from one or more monomers having the general formulae (II to VII):

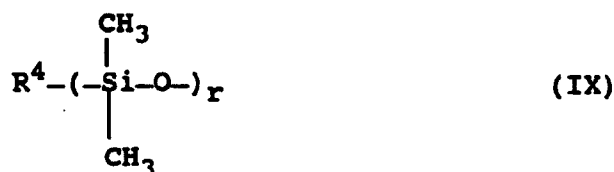




In these structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; X is



R¹ is hydrogen or -COOH (preferably R¹ is hydrogen); R² is hydrogen, methyl or -CH₂COOH (preferably R² is methyl); Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R⁴ is alkyl); and r is an integer from 5 to 700, preferably from 50 to 500, more preferably from 150 to 300. Of the above, formula II is preferred, particularly when p = 0 and q = 3.

The polymers utilized herein generally comprise from 0% to about 98% (preferably from about 5% to about 92%, more preferably from about

50% to about 90%) of monomer A, from about 1% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99.5%, most preferably from about 75% to about 98%) of the polymer.

Preferred silicone-containing copolymers for use herein are selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS)
macromer-20,000 molecular weight (mw) (10/70/20 w/w/w)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(20/60/20 w/w/w)

acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)

t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw
(60/20/20)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(10/70/20);

acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw
(40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw
(25/65/15);

acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw
(60/25/15);

acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

The silicone-containing copolymers described above can be synthesized by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179 - 318.

In compositions according to the invention it can be desirable to purify the silicone containing copolymer by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the T_g of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer is solubilized by supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurised and dry, extracted polymer is recovered from the extraction vessel.

Neutralising System

The hair styling polymers, herein are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. The present development relates to the neutralisation of a hair fixative polymer (eg silicone grafted tBA/AA copolymer) with a combination of neutraliser systems, specifically an inorganic base, preferably KOH, and an organic base, preferably AMP

(amino methyl propanol) in hairspray and other hair cosmetic products. In particular the present development relates to improving the clarity of hairspray and other hair cosmetic products containing low levels of water, approximately 0 - 10%, preferably 0 - 7% water. It has been discovered that addition of a very small % of organic base dramatically improves the solubility and clarity of low water containing hairspray products containing silicone-grafted copolymer. In addition use of organic base in these levels does not increase the sticky hair feel. This is surprising as neutralisation with AMP traditionally leads to sticky hair feel negatives. Additional benefits include improved hold via increased polymer bond flexibility whilst maintaining ease of wash-out and reduced negatives such as rough hair feel associated with inorganic (non-plasticising) neutralisers eg. KOH. Furthermore compositions according to the invention provide excellent hair conditioning benefits. In total from about 30% to about 95%, preferably from about 55% to about 75%, most preferably from about 60% to about 70% of the acidic monomers of the polymer should be neutralised.

Optimum neutralising systems for compositions according to the invention contain a mixture of inorganic and organic bases at a level sufficient to provide from about 25% to about 80%, preferably about 40% to about 70%, more preferably about 55% to about 65% neutralisation of the acid groups on the silicone containing copolymer with inorganic neutraliser and from about 0.01% to about 15%, preferably about 0.5% to about 8%, more preferably about 1% to about 6% neutralisation of the acid groups on the silicone containing copolymer with organic neutraliser. In preferred embodiments the weight ratio of inorganic base to organic base is in the range of from 1000 : 1 to 4 : 1, preferably from 100 : 1 to 5 : 1, more preferably from 50 : 1 to 6 : 1.

The particular effects of such systems are improved product clarity; improved solubility in ethanol; improved long term stability of the product and improved style retention via increased polymer bond flexibility.

Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers providing they are utilised in mixtures as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols

are suitable neutralisers for use in the present liquid hair cosmetic compositions.

Examples of suitable organic neutralising agents which may be included in the hair cosmetic compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethyl steramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in hairspray compositions of the present invention are potassium and sodium hydroxides and aminomethyl propanol (AMP).

The amount in grams of inorganic and organic base (Z) required to neutralise a polymer can be deduced from calculations which take into account the acid value of the polymer (A); amount of polymer (W); mol wt of the base (B); mol wt of the acidic moiety (M) and the degree of neutralisation required (N).

$$Z(g) = W \times A/100 \times 1/M \times B \times N\%$$

In the following example the amount of KOH required to neutralise 2.6g of acrylic acid co-polymer (with acid value of 20) to a level of 60% neutralisation is calculated.

$$Z(g) = 2.6 \times 20/100 \times 1/72 \times 56 \times 0.60$$

$$Z = 0.242 g$$

Note the acid value can be experimentally determined by titrating a specific amount of the polymer with base or theoretically by considering

the original acidic content of the co-polymer i.e. a polymer with 20% of acid monomer has an acid value of 20.

As described earlier herein, use of the herein defined mixed inorganic/organic neutralising system for at least partial neutralisation of the silicone grafted copolymer leads to liquid hair cosmetic compositions of dramatically improved clarity. Product clarity is measured using a Digital Direct Reading Turbidimeter. Using this equipment the turbidity of test samples is measured by calibration against two known references (Orbeco-Hellige Transfer Turbidity Standards) which give turbidity readings of 0 and 999 respectively. Typical turbidity measurement for opaque systems neutralised with inorganic neutraliser can be as high as 700.

In contrast the clarity of the mixed organic/inorganic neutralised systems according to the invention registers a turbidity measurement in the range from 0 to 50, preferable 0 to 40, more preferably 0 to 30.

The liquid hair cosmetic compositions of the present invention also include a carrier. This can comprise any of those conventionally used in resin hairspray formulations inclusive of solvents, propellants and other optional ingredients of liquid hair cosmetics. The carrier is generally present in the liquid hair cosmetic compositions at from about 70% to about 99.8%, preferably from about 78% to about 99% by weight. More preferably, the carrier is present at from about 80% to about 98% by weight of the total composition.

Organic solvents suitable for use in the carrier of the present compositions include C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof.

Liquid hair cosmetic compositions according to the present invention contain from 0% to about 10% by weight of water, preferably from 0% to about 7% by weight of water. It is a feature of the invention that utilising mixed neutraliser systems as defined herein, liquid hair cosmetic

compositions having excellent clarity are achieved at zero or low levels of water content.

Plasticizer

The performance of the liquid hair cosmetic compositions according to the invention can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at up to a level of 25%, preferable from 1% to 20%, more preferably from 1% to 15%. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapour pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the hair cosmetic carrier is evaporating, since this may excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and J. R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982). See especially in the Appendix of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

Plasticizers suitable for use in compositions of the present invention include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄ - C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutyrate, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates, camphor, glycols, amine derivatives, selected short chain alcohols and castor oil.

Particularly preferred plasticizers for use herein include glycol and citrate based plasticizers such as propylene glycol, dipropylene glycol ,

acetyl tri-n-butyl citrate, tri-n-butyl and acetyl tri-2-ethoxyhexyl citrate (as supplied by Pfizer under the trade name Citroflex RTM) and also glycerin, amino methyl propanol (AMP), diisobutyladipate (DIBA) and isopropanol.

Propellant

The present compositions can be formulated as hairsprays in aerosol or non-aerosol forms. If an aerosol hairspray is desired, a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hairspray character.

The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Preferably the density of the propellant or mixture thereof is less than 1 so that pure propellant is not emitted from the container. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether e.g. Dimel 152A (RTM) supplied by Du Pont, propane, n-butane, isobutane, used singly or admixed and propane butane e.g. CAP 80 (RTM). Dimel 152A (RTM) and propane butane are preferred.

The amount of the propellant gas is governed by normal factors well known in the aerosol art. For hairsprays the level of propellant is generally from about 10% to about 40%, preferably from about 20% to about 30%, of the total composition. If a propellant such as dimethylether utilizes vapor pressure suppressant (e.g., trichloroethane or dichloromethane) the amount of suppressant is included as part of the propellant.

The hair spray compositions of the present invention can be made using conventional formulation and mixing techniques. Compositions of the present invention can be made by adding the polymer to ethanol and mixing for several hours until dissolved. Plasticizer and neutralising ingredients are then added and the resulting solution is stirred. Any

remaining ingredients such as water, ethanol and perfume can then be added.

Methods of making the hair cosmetic compositions of the present invention are described more specifically in the examples.

Alternatively, pressurised aerosol dispensers can be used where the propellant is separated from contact with the hairspray composition by use of specialised containers such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in US-A-4,077,441, March 7th 1978, Olofsson and US-A-4,850,577, July 25th 1989, TerStegé. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY (RTM) hairsprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other Ingredients

The liquid hair cosmetic compositions of the present invention can also contain a variety of non-essential, optional components such as preservatives, surfactants, block polymers, thickeners and viscosity modifiers, electrolytes, fatty alcohols, pH adjusting agents, perfume oils, perfume solubilizing agents, sequestering agents; emollients; lubricants and penetrants such as various lanolin components; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; sunscreens and volatile and non-volatile silicone fluids. Such conventional optional ingredients are well known to a person skilled in the art, e.g. surfactants such as anionics (e.g., sodium alkyl sulphates, nonionics (amine oxides) ; amphoterics (aliphatic secondary or tertiary amine derivatives) zwitterionics (aliphatic quaternary ammonium; phosphonium or sulphonium derivatives) and fluorinated surfactants (e.g.

Zonyl FSK) (RTM); thickeners and viscosity modifiers such as diethanolamides of long chain fatty acids; block polymers of ethylene oxide and propylene oxide such as Pluronic (RTM) F88 offered by BASF Wyandotte; fatty alcohols such as cetearyl alcohol; viscosity modifiers such as sodium chloride, sodium sulphate, and ethyl alcohol; electrolyte such as earth and alkaline-earth metal salts; quaternary ammonium ions and cationic amines and halogen ions; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; perfume oils such as Florasynth (RTM) perfumes; perfume oil solubilizers such as polyethylene glycol fatty acid esters and sequestering agents such as ethylenediamine tetraacetic acid. Each of these optional materials can be present at a level of from about 0.05% to about 5%, preferably from about 0.1% to about 3% by weight of composition.

The liquid hair cosmetic compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits desired considering the length and texture of the hair.

The invention is illustrated by the following non-limiting examples.

In the examples, all concentrations are on a 100% active basis, unless otherwise stated and the abbreviations have the following designation:

Hair Styling Polymer - 60% t-butyl acrylate/20% acrylic acid/20% silicone PDMS. Weight average molecular weight (measured by SEC) of 150,000.

KOH - Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors.

AMP - 2-Amino-2-methyl-1-propanol.

DRO Water - Double reverse osmosis water

Solvent - Ethanol

Examples I-VI

The following are liquid hair cosmetic compositions in the form of hairspray compositions suitable for pump spray dispensers and which are representative of the present invention:

	I	II	III	IV	V	VI
Hair Styling Polymer	3.0	2.0	4.0	6.0	2.0	5.0
% poly KOH neutralised	60	55	60	65	60	55
% poly AMP neutralised	5	5	8	2	10	5
DRO Water	0	3.0	7.0	7.0	10.0	0
Balance	-----to 100 percent with ethanol-----					

The balance contains ethanol and optional ingredients such as plasticizer, perfume and surfactants.

The hairspray formulations are prepared by adding the polymer directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. The neutralizing agent (KOH and AMP) is then added and mixed into the premix. Then, the optional ingredients and water, as may be applicable, are mixed into the composition.

The above compositions provide effective style retention, deliver a hair conditioning effect and have excellent clarity.

Examples VII-XII

The following are liquid hair cosmetic compositions in the form of hairspray concentrate compositions suitable for aerosol dispensers and which are representative of the present invention:

	VII	VIII	IX	X	XI	XII
Hair Styling Polymer	4.0	2.0	5.0	6.0	3.0	7.0
% poly KOH neutralised	55	60	60	65	55	65
% poly AMP neutralised	5	8	2	2	5	5
DRO Water	0	7.0	10.0	7.0	0	0
Balance	----- to 100 percent with solvent -----					

As in examples I to VI the balance can contain ethanol and optional ingredients such as plasticizer, perfume and surfactants. The above compositions are prepared as in Examples I-VI. The concentrates are packaged in conventional aerosol spray cans and are charged with a conventional liquifiable propellant such as CAP 80 (RTM) at a propellant:concentrate weight ratio of 23:77.

The above compositions will have excellent clarity and stability characteristics and when applied to the hair, provide good hair styling and conditioning benefits.

WHAT IS CLAIMED IS:

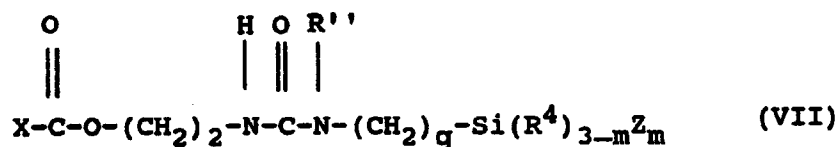
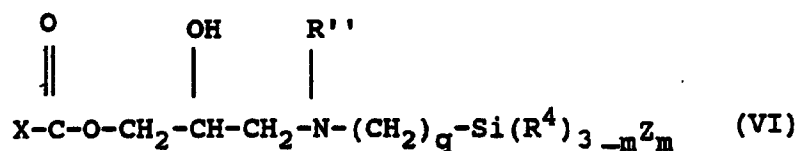
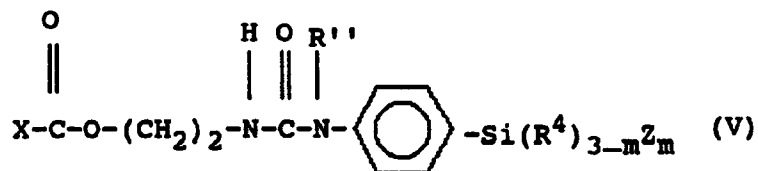
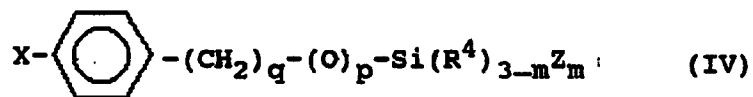
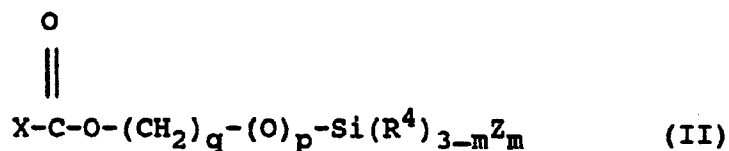
1. A liquid hair cosmetic composition comprising:-
 - (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% of the acid groups on the silicone-containing copolymer; and
 - (c) from 0% to about 10% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.
2. A liquid hair cosmetic composition according to Claim 1 wherein the silicone-containing macromer has the general formula (I):



wherein X is a vinyl group; Y is a divalent linking group; R is hydrogen, alkyl, aryl, alkylamino, trialkylsiloxy or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500; n is 0 or 1; and m is an integer from 1 to 3.

3. A liquid hair cosmetic composition according to Claim 1 or 2 wherein the silicone-containing copolymer has a weight average

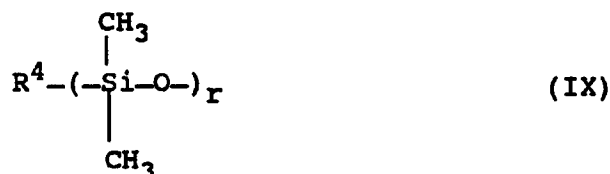
molecular weight of from 10,000 to 1,000,000 comprising a hydrophilic carboxylate containing monomer (B), optionally a lipophilic, low polarity, free-radically polymerizable vinyl monomer (A) which is copolymerizable with B, and a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, based on polydimethylsiloxane and wherein the macromer (C) is selected from one or more monomers having the general formulae (II - VII):



wherein m is 1, 2 or 3; p is 0 or 1; R" is alkyl or hydrogen; q is an integer from 2 to 6; X is



R¹ is hydrogen or -COOH; R² is hydrogen, methyl or -CH₂COOH; Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 1% to 98% monomer B, and from 0.1% to 50% monomer C.

4. A liquid hair cosmetic composition according to any of Claims 1 to 3 wherein the silicone-containing copolymer comprises from 5% to 92% by weight monomer A, from 7.5% to 80% by weight monomer B, and from 0.1% to 50% monomer C.
5. A liquid hair cosmetic composition according to any of Claims 1 to 4 wherein monomer A is selected from acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.
6. A liquid hair cosmetic composition according to any of Claims 1 to 5 wherein monomer B is selected from acrylic acid, methacrylic

acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid and mixtures thereof; and is preferably selected from acrylic acid and methacrylic acid and mixtures thereof.

7. A liquid hair cosmetic composition according to any of Claims 3 to 6 wherein the silicone containing macromer has the general formula (II) in which $p = 0$ and $q = 3$, m is 1, R^4 is alkyl, R^1 is hydrogen and R^2 is methyl.

8. A liquid hair cosmetic composition according to any of Claims 1 to 7 wherein the silicone-containing copolymer is selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 molecular weight (mw) (10/70/20);

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (20/60/20 w/w/w)

acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)

t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw (60/20/20)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);

acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/15);

acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw (60/25/15);

acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

9. A liquid hair cosmetic composition according to any of Claims 1 to 8 wherein the silicone-containing copolymer is neutralised to a level of from about 0.5% to about 8%, preferably from about 1% to about 6% with organic base and to a level of from about 40% to about 70%, preferably from about 55% to about 65% with inorganic base.

10. A liquid hair cosmetic composition according to any of Claims 1 to 9 wherein the silicone-containing copolymer is neutralised to a total level of from 30% to 95% , preferably from 55% to 75% , more preferably from 60% to 70% .
11. A liquid hair cosmetic composition according to any of Claims 1 to 10 wherein the weight ratio of inorganic base to organic base is in the range of from 1000:1 to about 4:1; preferably from 100:1 to 5:1, more preferably from 50:1 to 6:1.
12. A liquid hair cosmetic composition according to any of Claims 1 to 11 wherein the inorganic base is selected from alkali, alkaline earth and ammonium hydroxides and mixtures thereof, preferably potassium hydroxide or sodium hydroxide.
13. A liquid hair cosmetic composition according to any of Claims 1 to 12 wherein the organic base is selected from amines and amino alcohols and is preferably an amino alcohol selected from 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS) and mixtures thereof and is preferably amino methyl propanol.
14. A liquid hair cosmetic composition according to any of Claims 1 to 13 wherein the mixed inorganic/organic base neutralising system comprises potassium hydroxide and amino methyl propanol.
15. A liquid hair cosmetic product comprising a hairspray composition and spray dispenser means for containing and spraying the hairspray composition, and wherein the hairspray composition comprises:

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% , preferably from about 50% to about 70% of the acid groups on the silicone-containing copolymer;
- (c) from 0% to about 10% by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US94/05245
A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A61K 7/08, 7/48, 7/13

US CL :424/70, 71; 514/781

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70, 71

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,104,646 (BOLICH JR. ET AL) 14 April 1992, column 22, lines 15-65, column 23, lines 1-55, column 24, lines 1-25, column 25, lines 20-25, claims.	1-3, 15

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 SEPTEMBER 1994

Date of mailing of the international search report

21 OCT 1994

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US94/05245**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A61K 7/06	A1	(11) International Publication Number: WO 95/04518 (43) International Publication Date: 16 February 1995 (16.02.95)
(21) International Application Number: PCT/US94/08031 (22) International Filing Date: 19 July 1994 (19.07.94) (30) Priority Data: 08/102,433 5 August 1993 (05.08.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: MIDHA, Sanjeev; 9274 Deercross Parkway, Blue Ash, OH 45236 (US). TORGERSON, Peter, Marte; 4127 U.S. Route 35 NW, Washington Court House, OH 43160 (US). HALL, Christine; 6072 Dryden Avenue, Cincinnati, OH 45213 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HAIR STYLING COMPOSITIONS CONTAINING A SILICONE GRAFTED POLYMER AND LOW LEVEL OF A VOLATILE HYDROCARBON SOLVENT (57) Abstract Provided hair styling compositions comprising: (a) from about 0.1 % to about 15 %, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone; (b) from about 0.5 % to about 15 %, by weight, of a hydrocarbon solvent selected from the group consisting of C ₁₀ -C ₁₄ branched chain hydrocarbons, and mixtures thereof; (c) a polar solvent phase comprising from about 80 % to about 98.9 %, by weight of the composition, of a polar solvent selected from the group consisting of water and C ₂ -C ₃ monohydric alcohols, and mixtures thereof, wherein said composition contains no more than about 15 %, by weight, of C ₃ monohydric alcohol; wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent. In preferred embodiments, the compositions hereof additionally comprise a plasticizer for the silicone grafted hair setting polymer. Especially preferred plasticizers include acetyl tri-C ₂ -C ₃ alkyl citrates, particularly acetyl triethyl citrate.		

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HAIR STYLING COMPOSITIONS CONTAINING A SILICONE GRAFTED
POLYMER AND LOW LEVEL OF A VOLATILE HYDROCARBON
SOLVENT

5

10

TECHNICAL FIELD

The present invention relates to hair styling compositions containing a silicone organic polymer as a hair setting agent. More particularly, the present invention relates to hairs styling compositions containing a silicone grafted organic polymer, having an organic backbone that is soluble either in water, lower alkanol, or a mixture thereof, and further containing an insoluble hydrocarbon solvent.

15

BACKGROUND OF THE INVENTION

The desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousses, gels, lotions or sprays.

25

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as AMPHOMER^R, supplied by National Starch and Chemical Company, and GANTREZ^R SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

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Hair sprays have been conventionally formulated with high amounts of monohydric alcohol solvents, such as ethanol and isopropanol, and relatively low amounts of water since the presence of water adversely affects spray quality. However, it is now particularly
5 desirable to formulate hair spray compositions with reduced levels of volatile organic compounds, such as ethanol, isopropanol, and other volatile materials, such as aerosol propellants. One way to do this is to increase the levels of water in the formulations. In doing so, it would be highly desirable to provide reformulated products which overcome the
10 problems conventionally associated with the addition of water to hair spray products. In particular, higher levels of water can negatively impact hair feel.

Recently, it has become known to utilize silicone grafted organic backbone polymers as hair setting agents in hairspray compositions and
15 other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make hair spray compositions which provide hair setting ability with improved hair feel, e.g., increased softness relative to conventional polymeric hair setting agents.

20 However, it remains desirable to improve the hair feel performance these silicone grafted polymers can provide at a particular level of hair hold, or conversely, to improve hair hold (after application and drying of such compositions) for a particular level of hair feel performance. It is an object of this invention to provide hair spray
25 compositions, and other aqueous, alcohol, or hydroalcoholic-based hair setting solutions, containing silicone grafted organic backbone polymeric hair setting agents that provide such improved combinations of hair feel/hair hold performance.

It is a further object of this invention to provide hair setting
30 compositions, as described above, that provide both improved hair feel and improved hair hold ability for a particular level of silicone grafted polymer in the composition.

It is yet a further object of this invention to provide compositions that meet the above objects for conventional volatile organic solvent
35 level (conventional VOC) compositions, which typically contain greater than 80% of volatile organic compounds, as well as for reduced volatile

organic solvent level (reduced VOC) compositions, i.e., compositions having 80% or less volatile organic solvents.

These and other benefits as may be apparent from the description below can be obtained by the present invention.

5 The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

10 All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

 All ingredient levels are refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

15 SUMMARY OF THE INVENTION

 The present invention relates to hair styling compositions comprising:

- 20 (a) from about 0.1% to about 15%, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone;
- (b) from about 0.5% to about 15%, by weight, of a hydrocarbon solvent selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, having
25 a boiling point of from about 105°C to about 260°C;
- (c) a polar solvent phase comprising from about 80% to about 98.9%, by weight of the composition, of a polar solvent selected from the group consisting of water and C₂-C₃ monohydric alcohols, and mixtures thereof, wherein said
30 composition contains no more than about 15%, by weight, of C₃ monohydric alcohol;

 wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent.

35 In preferred embodiments, the compositions hereof additionally comprise a plasticizer for the silicone grafted hair setting polymer.

Especially preferred plasticizers include acetyl tri-C₂-C₈ alkyl citrates, particularly acetyl triethyl citrate.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described
5 below. Also included is a nonexclusive description of various optional
and preferred components useful in embodiments of the present
invention.

Silicone Grafted Adhesive Polymer

The compositions of the present invention essentially comprise a
10 silicone grafted adhesive polymer as a hair setting agent. The
compositions hereof will generally comprise from about 0.1% to about
15%, preferably from 0.5% to about 8%, more preferably from about 1%
to about 8%, by weight of the composition, of the silicone grafted
15 polymer. It is not intended to exclude the use of higher or lower levels of
the polymers, as long as an effective amount is used to provide adhesive
or film-forming properties to the composition and the composition can be
formulated and effectively applied for its intended purpose. By adhesive
polymer what is meant is that when applied as a solution to a surface and
20 dried, the polymer forms a film. Such a film will have adhesive and
cohesive strength, as is understood by those skilled in the art. .

The silicone grafted polymers are characterized by polysiloxane
moieties covalently bonded to and pendant from a polymeric carbon-
based backbone. The backbone will preferably be a carbon chain
derived from polymerization of ethylenically unsaturated monomers, but
25 can also be, cellulosic chains or other carbohydrate-derived polymeric
chains to which polysiloxane moieties are pendant. The backbone can
also include ether groups, i.e., C-O-C. The polysiloxane moieties can be
substituted on the polymer or can be made by co-polymerization of
polysiloxane-containing polymerizable monomers (e.g. ethylenically
30 unsaturated monomers, ethers, and/or epoxides) with non-polysiloxane-
containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average
molecular weight of at least about 20,000. There is no upper limit for
molecular weight except that which limits applicability of the invention for
35 practical reasons, such as processing, aesthetic characteristics,
formulateability, etc. In general, the weight average molecular weight will
be less than about 10,000,000, more generally less than about

5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

5 Preferably, the grafted-polymers hereof when dried to form a film have a Tg or Tm of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-polysiloxane backbone of the polymer, and the abbreviation "Tm" 10 refers to the crystalline melting point of the non-siloxane backbone, if such a transition exists for a given polymer. Preferably, both the Tg and the Tm, if any, are above about -20°C, more preferably above about 20°C.

15 The silicone grafted polymers for the compositions of the present invention include "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

20 The silicone grafted polymers should satisfy the following four criteria:

- (1) when dried the polymer phase-separates into a discontinuous phase which includes the polysiloxane portion and a continuous phase which includes the non-polysiloxane portion;
- 25 (2) the polysiloxane portion is covalently bonded to the non-polysiloxane portion; and
- (3) the molecular weight of the polysiloxane portion is at least about 500; and

30 When used in a composition, such as a personal care composition for application to the hair or skin, the non-polysiloxane portion should permit the polymer to deposit on the intended surface, such as hair or skin.

35 It is believed that the phase separation property provides a specific orientation of the polymer which results in the desired combination of tactile feel, and film-forming or adhesive benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a solvent (i.e., a solvent which dissolves both the backbone and the polysiloxane-graft portions). This film is then sectioned and examined by transmission electron microscopy. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein, said thesis incorporated by reference herein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

A third method for determining phase-separating characteristics is via Scanning Electron Microscopy (SEM), to examine the topographical morphology of dried film of the silicone grafted polymer. SEM can be used to demonstrate microphase separation at the surface of the polymer film by the observation of hemi-spherical discontinuities (typically hemi-spherical or hemi-conical) formed by the silicone macromer component grafted on the polymer backbone of the silicone grafter polymer.

The preferred silicone grafted polymers comprise an organic backbone preferably a carbon backbone derived from ethylenically unsaturated monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer (especially preferred are polydialkylsiloxane, most preferably polydimethylsiloxane) grafted to the backbone. The polysiloxane macromer should have a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more

preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those
5 that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc. Also contemplated are backbones based on cellulosic chains, ether-containing backbones, etc.

Examples of useful polymers and how they are made are
10 described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

Suitable silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on
15 January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial
20 No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable
25 ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

The silicone grafted polymers hereof generally comprise from about 1% to about 50%, by weight, of polysiloxane-containing monomer
30 units, i.e., monomer units polysiloxane-containing monomers (referred to herein as "C" monomers), and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers.

The non-polysiloxane-containing monomer units can be derived from polar, or hydrophilic, monomers, "A" monomers, or mixtures of polar
35 hydrophilic monomers and low polarity, or hydrophobic, "B" monomers.

Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers

means monomers which do not form substantially water insoluble homopolymers. Substantially water soluble shall refer to monomers that form homopolymers that are soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and are preferably soluble at 1.0% by weight. Substantially water insoluble shall refer to monomers that form homopolymers that are not soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and preferably not soluble at 0.1% by weight. The weight average molecular weight for purposes of determining substantial water solubility or insolubility shall be about 100,000, although solubility at higher molecular weight shall also be indicative of solubility at about 100,000.

The particular relative amounts of A, B, and C monomers can vary as long as the polymer backbone is soluble in the polar solvent hereof and the silicone grafted copolymer exhibits phase separation when dried.

Representative examples of A monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, salts of any acids and amines listed above, and mixtures thereof. Preferred A monomers include acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

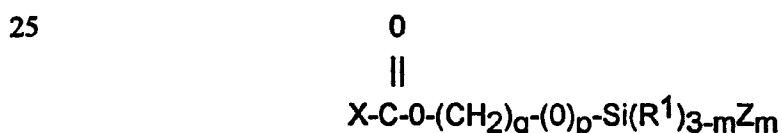
Representative examples of B monomers are acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-

hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred B monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, B is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

Polymerizable polysiloxane-containing monomers (C monomer) are exemplified by the general formula:



wherein X is an ethylenically unsaturated group copolymerizable with the A and B monomers, such as a vinyl group; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:

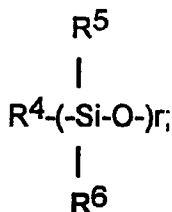


In this structure, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R¹ is alkyl); X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is

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10 R^4 , R^5 , and R^6 independently are lower alkyl, alkoxy, alkylamino, aryl, aryl, hydrogen or hydroxyl (preferably R^4 , R^5 , and R^6 are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R^4 , R^5 , and R^6 are methyl, $p=0$, and $q=3$.

15 In general, the silicone grafted polymer will preferably comprise from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95%, by weight of the polymer, of non-silicone macromer-containing monomer units, e.g. the total A and B monomer units, and from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of silicone macromer-containing monomer units, e.g. the C monomer units. The level of A monomer units can be from about 1% to about 99%, preferably from about 5% to about 80%, more preferably from about 10% to about 50%, most preferably from about 15% to about 40%; the level of B monomer units, can be from 0% to about 99%, preferably from about 1% to about 90%, more preferably from about 5% to about 85%, most preferably from about 15% to about 80%; and the level of C monomer units, from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%.

25 The composition of any particular silicone grafted polymer will help determine its formulational properties. By appropriate selection and combination of particular A, B and C components, the silicone grafted polymer can be optimized for inclusion in specific vehicles. The backbone of the silicone grafted polymer included in the compositions hereof must be soluble in the polar solvent, which is hereinafter referred to as the silicone grafted polymer, as a whole, being soluble in the polar solvent. This is determined according to whether the polymer can stay in solution or precipitates out of solution at 25°C at the concentration present in the composition or whether the range of concentrations for silicone grafted polymer described herein. It is well within the skill of one

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in the art to select monomers for incorporation into the polymers for formulateability and solubility in selected polar solvent systems.

Exemplary silicone grafted polymers for use in the present invention include the following:

- 5 (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer 20,000 molecular weight macromer
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight macromer
- 10 (iii) t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight macromer
- (iv) t-butylacrylate/acrylic acid/PDMS macromer-20,000 molecular weight macromer

15 The silicone grafted polymers can be synthesized by free radical polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, 20 along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. 25 The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. 30 The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer can be further purified, as desired.

 In particular the silicone grafted polymers can be purified by removing unreacted silicone-containing monomer and silicone 35 macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent hexane

extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room
5 temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

As an alternative to a batch reaction, the silicone grafted polymer
10 can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers is made during the polymerization reaction. This is advantageous when the polymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at
15 the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction. Typically, the silicone macromer-
20 combining monomers, the "C" monomers as described above, will react more slowly than the non-silicone macromer-containing monomers. To compensate for this, for example, more consistent distribution of C monomer can be obtained by adding all the C monomer and half of the A and B monomers in the first addition of monomers to the reaction, and
25 the rest of the A and B monomers in a second addition.

As is known in the art, polymers which have acidic functionalities, such as carboxyl groups, are usually used in at least partially neutralized form to promote solubility/dispersibility of the polymer. In addition, use of the neutralized form aids in the ability of the hair care compositions to be
30 removed from the hair by shampooing. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, of the acidic monomers of the polymer be neutralized.

Any conventionally used base, organic or metallic, may be used
35 for neutralization of the polymers. Metallic bases are particularly useful in the present compositions. Hydroxides, where the cation is an alkali

metal or an alkaline earth metal, are suitable neutralizers for use in the present hair spray compositions.

Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide.

5 Examples of other suitable neutralizing agents which may be included in the hair spray compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB),
10 monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanol-amine (DIPA), tri-isopropanolamine (TIPA) and dimethyl steramine (DMS). Particularly useful neutralizing agents are mixtures of amines and metallic bases.

15 Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrogen chloride.

 Solubility of the silicone grafted polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase,
20 such as surfactants, solubilizers, etc.

Polar Solvent Phase

 The liquid care compositions of the present invention also include a polar solvent phase as a liquid vehicle for the silicone grafted polymer. The polar solvent phases comprise one or more polar solvents that are
25 present in the hair care compositions at a level of from about 80% to about 98.9%, preferably from about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

 The polar solvents essential to the present compositions are selected from the group consisting of water C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol,
30 should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they
35 can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the reduced volatile organic solvent hair styling products hereof, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

Nonpolar, Branched Chain Hydrocarbon

The compositions hereof contain as an essential element a volatile, nonpolar, branched chain hydrocarbon, which acts as a solvent for the silicone portion of the silicone grafted copolymer and is safe for topical application to the skin and hair. The branched chain hydrocarbon solvent hereof is present at a level of from about 0.5% to about 15%, preferably from about 1% to about 10%, more preferably from about 2% to about 8%, by weight of the composition.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C,

more preferably at least about 125°C, most preferably at least about 150 °C . The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

5 The branched chain hydrocarbon solvents are selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, preferably C₁₁-C₁₃ branched chain hydrocarbons, more preferably C₁₂ branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it isn't necessarily intended to exclude
10 unsaturated hydrocarbons.

 Examples of suitable nonpolar solvents include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include IsoparTM G (C₁₀-C₁₁ isoparaffins), IsoparTM H and K (C₁₁-C₁₂ isoparaffins), and IsoparTM L (C₁₁-C₁₃
15 isoparaffins). The most preferred nonpolar solvent are C₁₂ branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as PermethylTM 99A.

 The silicone macromer portion of the silicone grafted polymer is
20 soluble in the nonpolar hydrocarbon solvent in the present compositions. This can be easily determined by verifying whether a silicone macromer of the same composition and molecular weight as that grafted to the silicone grafted polymer is soluble in the nonpolar hydrocarbon solvent. In general, the macromer should be soluble at 25°C at a concentration of
25 0.1% by weight of the hydrocarbon solvent, preferably at 1%, more preferably at 5%, most preferably at 15%.

 The nonpolar hydrocarbon solvent, however, is insoluble in the polar solvent of the composition. This is determined in the absence of the silicone grafted polymer, or other emulsifying agents, and can easily
30 be verified by observing whether the polar and nonpolar solvents form separate phases after being mixed together.

 Without intending to be necessarily limited by any particular theory, it is believed that the nonpolar hydrocarbon solvent solubilizes the silicone macromer portion of the silicone grafted polymer. This is
35 believed to aid in obtaining a smoother polymer film upon drying. Since the hydrocarbon solvent is less volatile than the polar solvent phase, the hydrocarbon solvent maintains the silicone portions in solubilized form

for a relatively long period as the composition dries, thus minimizing aggregation of the silicone portions and, therefore, allowing the polymer to dry as a smoother film.

Plasticizer

5 The compositions hereof can optionally contain a plasticizer for the silicone grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

15 In a highly preferred embodiment hereof, surprising improvements in hair hold performance can be obtained when the present compositions have included therein certain plasticizers selected from the group consisting of acetyl tri-C₂-C₈ alkyl citrates, such as acetyl triethyl citrate. Other suitable examples include the tri-propyl, -butyl, -pentyl, etc., analogues of acetyl triethyl citrate.

20 Whereas it has been found that plasticizers of this type result in a brittle, gritty film of the silicone grafted polymer when formed from a composition not including the hydrocarbon solvent of the present invention, the use of the acetyl tri-alkyl citrate in the presence of the hydrocarbon solvent in the present compositions can provide improved hair hold relative to the citrate-free composition, without causing the hair to feel brittle or gritty, and while also allowing the hair to exhibit improved softness and comb-ability relative to a citrate plasticizer-containing composition that does not contain the nonpolar hydrocarbon solvent hereof.

25 The acetyl tri-alkyl citrate plasticizer hereof is generally used at a level of from about 0.025% to about 2%, preferably from about 0.05% to about 1%, by weight of the composition. Preferably, the weight ratio of silicone grafted polymer to the acetyl tri-alkyl citrate is from about 1:1 to about 40:1, preferably from about 10:1 to about 30:1, more preferably from about 15:1 to about 25:1.

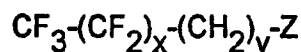
35 Optional Ingredients

 The present compositions can contain a wide variety of optional ingredients, including among them any of the types of ingredients known

in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and silicone copolyols, and silicone tonic strength modifiers, non-silicone grafted film-forming polymers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

Fluorosurfactants

Fluorosurfactants useful in the present compositions include perfluorinated compounds which can be represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Suitable anionic fluorosurfactants can have anionic moieties which include carboxylates, sulfates, sulfonates, phosphonates and phosphates or any combination thereof. Counterions therefore can include sodium, NH_4 , magnesium, potassium, tri-ethanolamine, di-ethanolamine, and similar moieties. Suitable cationic fluorosurfactants can have cationic moieties which include quaternary ammonium compounds where the counterions can be chloride or any other halide, methosulfate, ethosulfate, phosphate, acetate, and other similar moieties. Also, suitable cationic fluorosurfactants can have cationic moieties which include primary, secondary and tertiary amine salts of acids such as hydrochloric, lactic, phosphoric, sulfuric and other similar acids.

Also suitable for use are amphoteric fluorosurfactants, such as Fluorad FC-100® supplied by 3M; and the experimental amphoteric

fluorosurfactant L-12231 supplied by 3M; and also include zwitterionic fluorosurfactants such as those conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_3-8$ such as Zonyl FSK® supplied by DuPont.

- 5 Fluorosurfactant, are typically used at levels of from about 0.01% to about 2%, preferably from about 0.01% to about 1.5%. More preferably from about 0.02% to about 1%.

Non-fluorinated Surfactants

- 10 Optionally, the hair spray compositions can contain one or more non-fluorinated surfactant. Generally, if used such non-fluorinated surfactants will be used at a total level of from about 0.01% to about 2%, preferably from about 0.01% to about 1.5% and more preferably from about 0.01% to about 1%, by weight of the composition.

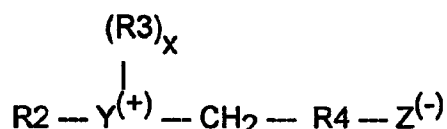
- 15 A wide variety of non-fluorinated surfactants can be used, including anionic, cationic, amphoteric, and zwitterionic surfactants.

- 20 Anionic surfactants include, for example: alkyl and alkenyl sulfates; alkyl and alkenyl ethoxylated sulfates; (preferably having an average degree of ethoxylation of 1 to 10), succinamate surfactants, such as alkylsulfosuccinamates and dialkyl esters of sulfosuccinic acid; neutralized fatty acid esters of isethionic acid; and alkyl and alkenyl sulfonates, including, for example, olefin sulfonates and beta-alkoxy alkane sulfonates. Preferred are alkyl and alkenyl sulfates and alkyl and alkenyl ethoxylated sulfates such as the sodium and ammonium salts of C_{12} - C_{18} sulfates and ethoxylated sulfates with a degree of ethoxylation of from 1 to about 6, preferably from 1 to about 4, e.g., lauryl sulfate and laureth (3.0) sulfate.

- 30 Amphoteric surfactants include those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent
- 35

2,528,378. Others include alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphoglycinates; alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphopropionates; and mixtures thereof.

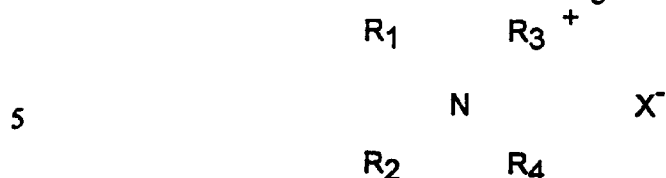
Suitable zwitterionic surfactants for use in the present compositions can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is sulfur or phosphorus, 1 or 2 when Y is nitrogen; R4 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups. Classes of zwitterionics include alkyl amino sulfonates, alkyl betaines, and alkyl amido betaines.

Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., **McCutcheon's, Detergents & Emulsifiers**, (North American edition 1979); Schwartz, et al., **Surface Active Agents, Their Chemistry and Technology**, New York: Interscience Publishers, 1949; U.S. Pat. No. 3,155,591, Hilfer, issued Nov. 3, 1964; U.S. Pat. No. 3,929,678, Laughlin, et al., issued Dec. 30, 1975; U.S. Pat. No. 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Pat. No. 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁ is an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R₂ is an aliphatic group having from 1 to 22 carbon atoms; R₃ and R₄ are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups. Other quaternary ammonium salts useful herein are diquaternary ammonium salts.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactants for use herein. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Pat. No. 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein).

Suitable cationic surfactant salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts.

Nonionic surfactants can also be included in the compositions hereof. Preferably, the nonionic surfactants have an average HLB (Hydrophile-Lipophile Balance) of less than or equal to about 7.

Methods of determining HLB are well known in the art and any of such methods may be used for HLB determination. A description of the HLB System and methods for HLB determination are described in "The

HLB System: a time saving guide to emulsifier selection, " ICI Americas Inc.; Wilmington, Delaware; 1976.

Nonionic surfactants include polyethylene oxide condensates of alkyl phenols (preferably C₆-C₁₂ alkyl, with a degree of ethoxylation of about 1 to about 6), condensation products of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, condensation products of aliphatic alcohols with ethylene oxide, long chain (i.e., typically C₁₂-C₂₂) tertiary amine oxides, long chain tertiary phosphine oxides, dialkyl sulfoxides containing one long chain alkyl or hydroxy alkyl radical and one short chain (preferably C₁-C₃) radical, silicone copolyols, and C₁-C₄ alkanol amides of acids having a C₈-C₂₂ acyl moiety.

Ionic Strength Modifier System

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier

system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl

sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

10 The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

Hair Styling Compositions

15 The present invention encompasses a wide variety of hair styling compositions, including hair spray compositions, mousses, and hair setting tonics. In general, the compositions will be flowable, low viscosity compositions that, preferably, are suitable for spray application. Higher viscosity compositions are also contemplated, however.

20 Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

25 When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

30 Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of
35 propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas.

The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents sunscreens; preservatives;

thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

METHOD OF MAKING

The hair styling compositions of the present invention can be made using conventional formulation and mixing techniques. Preferably, a premix of the silicone grafted polymer and the ethanol is made first. If ethanol is not to be used in the composition, a premix of the polymer with C₃ alkanol or water is prepared. The other ingredients can then be added with mixing to provide a homogeneous mixture. If the polymer is neutralized, the neutralizer is preferably added to the premix prior to addition of other ingredients.

METHOD OF USE

The compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves application of an effective amount of the product to dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the hair hold and style benefits desired considering the length and texture of the hair. In general, from about 0.5g to about 30g of product will be applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, and type of hair style.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTALS

The following synthesis exemplify silicone grafted polymers useful in the present compositions.

Experimental 1: Batch synthesis

Place 20 parts acrylic acid, 60 parts t-butyl acrylate, and 20 parts polysiloxane (10,000 MW) -containing monomer in a flask. Add sufficient ethyl acetate or acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Add initiator, (2,2'-azobis-(2,4-dimethylvaleronitrile)) to a level appropriate for the desired molecular weight. Typically this is in the range of 0.5% to 1.0% by weight relative to

the amount of monomer. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature. The polymer is purified by drying off the reaction solvent in an oven, or if acetone is used as the solvent precipitating the polymer, by adding water and then drying the precipitate.

Experimental 2: Semi-continuous synthesis

Place 20 parts acrylic acid, 60 parts t-butyl acrylate, and 30 parts polysiloxane (10,000 MW) -containing monomer in a flask. Add 300 parts ethyl acetate or acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with an inert atmosphere, e.g. nitrogen or argon. Add initiator, (2,2'-azobis-(2,4-dimethylvaleronitrile)) as in Experimental 1. Heat to 60°C and maintain this temperature. After polymerization of these monomers has proceeded about 15 minutes to about 1 hour, e.g. about 30 minutes, add a second monomer charge of 20 parts acrylic acid and 60 parts t-butyl acrylate, to give a final total monomer charge of approximately 40% by weight. Maintain at temperature for 48 hours. Terminate the reaction and purify the polymer as in Experimental 1.

EXAMPLES

Examples 1-6

The following examples represent nonaerosol hairspray compositions of the present invention.

Component (wt. %)	Example No					
	1	2	3	4	5	6
Silicone Grafted Polymer ¹	4.00	4.00	4.50	4.50	4.50	4.50
Isododecane ²	3.00	3.00	3.00	3.00	5.00	5.00
Acetyl triethyl citrate ³	0.20	--	0.22	--	--	--
Diisopropyl butyl adipate	--	--	--	0.22	0.32	--
Potassium hydroxide	0.40	0.40	0.45	0.45	0.44	0.44
Perfume	0.10	0.10	0.20	0.20	0.20	0.20
Water	16.00	16.10	7.00	7.00	15.54	15.86
Ethanol ⁴	75.30	75.50	84.62	84.63	74.00	74.00

¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ CITROFLEX A-2, from Morflex, Inc., Greensboro, NC, USA.

⁴ SDA 40 (100% ethanol).

5

Examples 7-10

The following examples represent aerosol hairspray compositions of the present invention.

Component (wt.%)	Example No.			
	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
10 Silicone Grafted Polymer ¹	3.50	3.50	3.50	3.50
Isododecane ²	3.00	3.00	3.00	3.00
Acetyl triethyl citrate ³	0.18	0.18	--	--
Diisopropyl butyl adipate	--	--	--	0.18
15 Potassium hydroxide	0.33	0.33	0.33	0.33
Perfume	0.10	0.10	0.10	0.10
Water	5.00	20.98	5.00	5.00
Ethanol ⁴	64.89	64.89	65.07	64.89
Propellant-Isobutane	7.02	7.02	7.02	7.02
20 Propellant-Hydrofluorocarbon 152a	15.98	--	15.98	15.98

¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

25 ² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ CITROFLEX A-2, from Morflex, Inc., Greensboro, NC, USA.

⁴ SDA 40 (100% ethanol).

30 In Examples 1-10, the compositions are prepared as described above, by first preparing a polymer premix with the ethanol, neutralizing the polymer with the potassium hydroxide (added as a 45% aqueous solution), then adding sequentially (as applicable) with mixing, water, isododecane, plasticizer, and perfume. Propellants for aerosol compositions are charged to conventional aerosol containers after the
35 remainder of the prepared composition has been added.

EXAMPLE 11

A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
5	Ethanol, 200 proof	75.92%
	Isopropanol	10.00%
	Silicone Graft Polymer ¹	3.00%
	KOH (45%) ²	0.88%
	DRO Water ³	7.00%
10	Isododecane	3.00%
	Fluorad FC-109R (25%) ⁴	0.20%

1 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 690,000.

15 2 Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors, supplied by Fisher Scientific.

3 Double reverse osmosis water

4 Fluorad FC-109R supplied by 3M containing 25% potassium fluoroalkyl carboxylates (an anionic fluorosurfactant), 12% propanol, 2% ethanol and 61% water and minors.

20 The hair spray formulation of Example II is prepared by preparing a premix of the resin in isopropanol. The isopropanol premix is added to the ethanol and then neutralized with the potassium hydroxide solution. Then, a premix of the fluorosurfactants and water is prepared and added to the neutralized premix. Isododecane is then added. Other adjuvants, such as fragrances, may then be added. A magnetic or air driven stirrer is used to mix the ingredients until the resin is dissolved.

EXAMPLE 12

30 A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	84.45%
	Silicone Graft Polymer ¹	3.00%
	KOH (45%)	0.88%
35	DRO Water	7.00%
	Isododecane	5.00%
	Zonyl FSK ^R (47%) ²	0.11%

1 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 690,000.

2 Zonyl FSK^R containing 47% fluorosurfactants conforming to the
5 formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and 53% Acetic Acid and minors, having a zwitterionic character, supplied by DuPont.

This composition is prepared as in Example 11.

EXAMPLE 13

10 A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	76.10%
	Isopropanol	10.40%
15	Silicone Grafter Polymer ¹	2.60%
	KOH (45%)	0.75%
	DRO Water	7.00%
	Isopar TM H (Exxon Chemical) ²	3.00%
	Fluorad FC-120 ^R (25%) ³	0.10%
20	Zonyl FSK (47%)	0.05%

1 60% t-butyl acrylate /20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 800,000.

2 IsoparTM H is a C₁₁₋₁₂ Isoparaffin

25 3 Fluorad FC-120^R supplied by 3M, having an anionic character and containing 25% mixed ammonium perfluoroalkyl sulfonates, 37.5% ethanol, and 37.5% water and minors.

This composition is prepared as in Example 11, substituting Isopar H for isododecane during processing.

30 EXAMPLE 14

A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
35	Ethanol, 200 proof	75.86%
	Isopropanol	10.40%
	Silicone Grafted Polymer ¹	2.60%

30

	KOH (45%)	0.69%
	DRO Water	7.00%
	Isopar TM L (Exxon Chemical) ²	3.00%
	Fluorad FC-120 ^R (25%)	0.40%
5	Zonyl FSK ^R (47%)	0.05%
1	60% t-butyl acrylate /20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 1,700,000.	
2	Isopar TM L is a C ₁₁₋₁₃ Isoparaffin	
10	This composition is prepared as in Example 13.	

EXAMPLE 15

A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
15	Ethanol, 200 proof	86.55%
	Silicone Grafted Polymer ¹	2.60%
	KOH (45%)	0.75%
	DRO Water	7.00%
	Isopar TM M(Exxon Chemical) ²	3.00%
20	Fluorad FC-135 ^R (50%) ³	0.10%
1	60% t-butyl acrylate/20% acrylic acid/20% silicone macromer weight average mw=20,000, having a weight average molecular weight of about 800,000.	
2	Isopar TM M is a C ₁₃₋₁₄ Isoparaffin	
25	3 Fluorad FC-135 ^R supplied by 3M, having anionic character and containing 25% mixed ammonium perfluoroalkyl sulfonates, 37.5% ethanol and 37.5% water and minors.	

This composition is prepared as in Example 13.

What is claimed is:

1. A Hair styling composition characterized in that it comprises:

- (a) from 0.1% to 15%, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone;
- (b) from 0.5% to 15%, by weight, of a hydrocarbon solvent selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof having a boiling point of from 105°C to 260°C;
- (c) a polar solvent phase comprising from 80% to 98.9%, by weight of the composition, of a polar solvent selected from the group consisting of water and C₂-C₃ monohydric alcohols, and mixtures thereof, wherein said composition contains no more than 15%, by weight, of C₃ monohydric alcohol;

wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent.

2. A hair styling composition as in Claim 1, wherein said composition comprises:

- (a) from 0.5% to 8%, by weight, of said silicone grafted polymer;
- (b) from 1% to 10%, by weight, of said hydrocarbon solvent;
- (c) from 85% to 98%, by weight, of said polar solvent, wherein said composition contains no more than 12%, by weight, of C₃ monohydric alcohol.

3. A hair styling composition as in Claim 1, wherein said composition comprises:

- (a) from 1% to 8%, by weight, of said silicone grafted polymer;
- (b) from 2% to 8%, by weight, of said hydrocarbon solvent;
- (c) from 80% to 98.9%, by weight, of said polar solvent, wherein said composition contains no more than 12%, by weight, of C₃ monohydric alcohol and said composition contains at least 10%, by weight, of water and no more than 80%, by weight, of volatile organic compounds.

4. A hair styling composition as in Claim 1, 2, or 3, wherein said silicone grafted polymer comprises from 50% to 99%, preferably from 75% to 95%, by weight, of non-silicone macromer-containing monomer units and from 1% to 50%,

preferably from 29% to 25%, by weight of silicone macromer-containing monomer units.

5. A hair styling composition as in Claim 4, wherein said silicone grafted polymer comprises from 1% to 99%, preferably from 15% to 40%, by weight, of hydrophilic monomer units and from 0% to 99%, preferably from 15% to 80%, by weight, of hydrophobic monomer units.

6. A hair styling composition as in Claim 5, wherein said hydrophilic monomer units are selected from the group consisting of acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines thereof, and mixtures thereof.

7. A hair styling composition as in Claim 6, wherein said hydrophobic monomer units are selected from the group consisting of n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof, preferably selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

8. A hair styling composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said hydrocarbon solvent is selected from the group consisting of saturated C₁₁-C₁₃ branched chain hydrocarbons, preferably isododecane.

9. A hair styling composition as in Claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein said composition further comprises a plasticizer selected from the group consisting of acetyl tri-C₂-C₈alkyl citrates, and mixtures thereof, preferably acetyl triethyl citrate.

10. A hair spray composition comprising a composition as in Claim 1, 2, 3, 4, 5, 6, 7, 8, Or 9, disposed within a hair spray dispenser.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 94/08031

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 408 311 (MITSUBISHI) 16 January 1991 cited in the application ---	1-10
Y	WO,A,93 03704 (PROCTER & GAMBLE) 4 March 1993 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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information on patent family members

Inter. Application No

PCT/US 94/08031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0408311	16-01-91	JP-A- 3128909 US-A- 5166276	31-05-91 24-11-92
WO-A-9303704	04-03-93	AU-A- 2502892 CA-A- 2115154 EP-A- 0600008 FI-A- 940771	16-03-93 04-03-93 08-06-94 18-02-94



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(21) International Application Number: PCT/US95/04756 (22) International Filing Date: 18 April 1995 (18.04.95) (30) Priority Data: 9410783.6 28 May 1994 (28.05.94) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): COOPER, Elizabeth, Claire [GB/GB]; 27 Heath Gardens, Twickenham, Middlesex TW1 4LY (GB). WELCH, Rosemary, Janue [GB/GB]; 15 Thomcroft, Englefield Green, Surrey TW20 0SB (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIR COSMETIC COMPOSITIONS (57) Abstract <p>A liquid hair cosmetic composition comprising: (a) from about 0.1 % by weight to about 10 % by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000; (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25 % of the acid groups on the silicone-containing copolymer; (c) from 0 % to about 1.0 % by weight of water; and (d) the balance comprising a carrier suitable for application to hair. The liquid hair cosmetic products have improved clarity and storage stability and demonstrate excellent hair styling benefits in addition to hair feel attributes and ease of removal and brush out.</p>		

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HAIR COSMETIC COMPOSITIONS

Technical Field

The present invention relates to hair cosmetic compositions. More particularly, this invention relates to liquid hair cosmetic compositions containing silicone-grafted hair styling polymers having improved long term product stability, hair feel attributes and ease of removal and brush out as well as excellent style retention properties.

Background Of The Invention

The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style retention is typically achieved by the use of resins, such as AMPHOMER, supplied by National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hairspray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000.

When such resins are incorporated into pump and aerosol hairsprays, they can provide suitable style retention attributes. However, such resins are found to be deficient in the area of hair feel and can give a stiff hair feel.

Recently, it has been found that certain neutralisable polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins without the tacky hair feel traditionally associated with non-silicone hair fixative polymers. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EP-A-0,408,311 A2 issued January 11th 1991, Hayama, et al., US-A-5,061,481, issued October 29th 1991, Suzuki et al., US-A-5,106,609, Bolich et al., issued April 21st 1992, US-A-5,100,658, Bolich et al., issued March 31st 1992, US-A-5,100,657, Ansher-Jackson, et al., issued March 31st 1992 and US-A-5,104,646, Bolich et al., issued April 14th 1992.

It is well known that at least partial neutralisation of the silicone macromer-containing hair styling polymer is necessary to maximise its utility in hair styling compositions. Typically, silicone grafted co-polymers neutralised with potassium hydroxide exhibit good solubility in hairspray compositions containing 15% water. However, potassium hydroxide neutralised systems are less soluble in compositions which contain lower levels of water and lead to hazy, colloidal systems. Moreover, silicone grafted co-polymers which are neutralised with organic neutralisers are found to lead to a somewhat tacky hair feel and are not easily removed from the hair by washing or brush-out.

Thus a need exists for hair styling compositions which have a clear appearance, deliver effective style retention, impart a hair conditioning effect, have a non-sticky hair feel, are easily brushed out and at the same time have stable product and viscosity characteristics and remain fully stable under long term and stressed temperature storage.

Summary of the Invention

According to one aspect of the invention, there is provided a liquid hair cosmetic composition comprising:-

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25 % of the acid groups on the silicone-containing copolymer;
- (c) from 0 % to about 1.0 % by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

The essential, as well as the optional, components of the present invention are described below. All levels and ratios are on a weight basis unless otherwise specified.

The compositions of the present invention contain from about 0.1 % to about 10.0%, preferably from about 0.5% to about 8.0% and especially from about 1 % to about 6% of specifically defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers preferably have a weight average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000, most preferably from about 90,000 to about 300,000 and, preferably, have a T_g of at least about -20°C. As used herein, the abbreviation "T_g" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "T_m" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

The molecular weights and molecular weight distributions of the polymers utilised in the compositions according to the present invention are determined by Size Exclusion Chromatography (SEC). In practise, polymers comprise a distribution of molecular weight species that gives rise to their unique properties. Separation of the molecules is accomplished by Size Exclusion Chromatography (SEC) using a crosslinked polystyrene -divinylbenzene column (MW range = $100 - 10^7$) with a differential refractive index detector and a differential viscometer. A universal calibration curve is prepared from monodispersed polystyrene standards of known molecular weight (MW) and molecular weight distribution (MWD). MW and MWD of the given polymer are determined based on concentration and viscosity responses relative to the calibration.

Preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg above about -20°C and, grafted to the backbone, a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the silicone containing macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits.

In its broadest aspect, the copolymers utilized in the present application comprise a silicone-containing monomer (hereafter identified as C) together with a hydrophilic carboxylate-containing monomer (B) and optionally a lipophilic monomer (A).

Examples of useful copolymers and their preparation are described in detail in US-A-4,693,935, Mazurek, issued September 15th 1987, and US-A-4,728,571, Clemens et al., issued March 1st 1988. These copolymers comprise monomers A, B and C as defined above. In preferred embodiments, A comprises at least one free radically polymerizable vinyl monomer or monomers and B comprises at least one

reinforcing monomer copolymerizable with A and selected from the group consisting of carboxylate-containing monomers and macromers having a T_g or a T_m above about -20°C. B can be up to about 98%, preferably up to about 80%, more preferably up to about 30%, of the total monomers in the copolymer. Monomer C comprises from about 0.1% to about 50.0% of the total monomers in the copolymer.

Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol (2-methyl-1-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

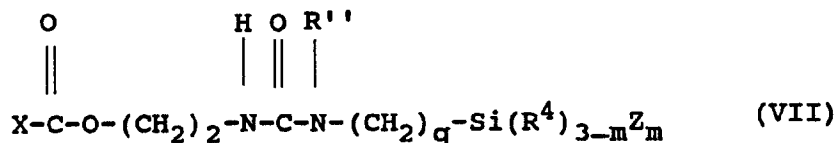
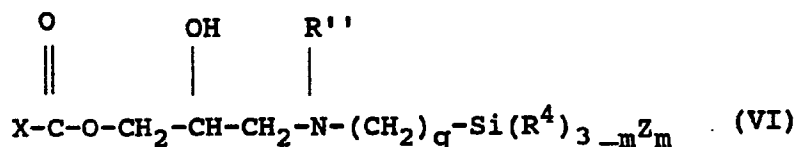
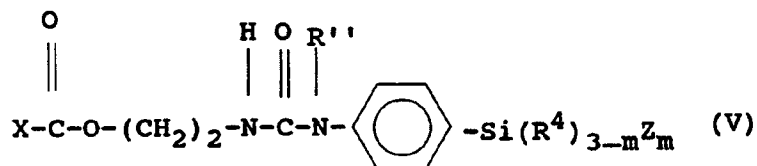
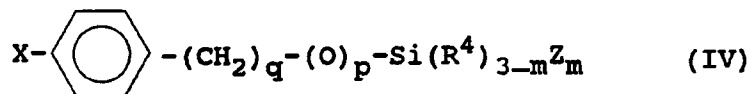
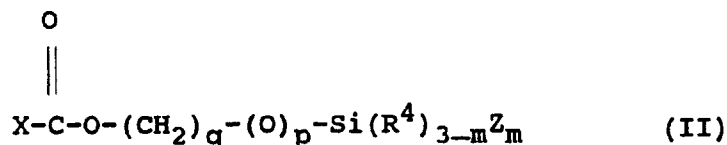
Representative examples of B (hydrophilic) neutralisable monomers containing a carboxyl moiety include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, and itaconic acid. Preferred B monomers include acrylic acid and methacrylic acid and mixtures thereof.

The C monomer preferably has the general formula (I):



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is hydrogen, C₁-C₄ alkyl, aryl, alkyl

amino, tri(C₁-C₄ alkyl)siloxy or C₁-C₄ alkoxy; Z is a monovalent siloxane polymeric moiety; n is 0 or 1; and m is an integer from 1 to 3. C has a number average molecular weight of, at least 500, preferably from 1,000 to 50,000. Preferably, the C monomer is selected from one or more monomers having the general formulae (II to VII):



In these structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; Rⁿ is alkyl or hydrogen; q is an integer from 2 to 6; X is



R^1 is hydrogen or $-\text{COOH}$ (preferably R^1 is hydrogen); R^2 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$ (preferably R^2 is methyl); Z is



R^4 is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R^4 is alkyl); and r is an integer from 5 to 700, preferably from 50 to 500, more preferably from 150 to 300. Of the above, formula II is preferred, particularly when $p = 0$ and $q = 3$.

The polymers utilized herein generally comprise from 0% to about 98% (preferably from about 5% to about 92%, more preferably from about 50% to about 90%) of monomer A, from about 1% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99.5%, most preferably from about 75% to about 98%) of the polymer.

Preferred silicone-containing copolymers for use herein are selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS)
macromer-20,000 molecular weight (mw) (10/70/20 w/w/w)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(20/60/20 w/w/w)

acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)

t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw
(60/20/20)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(10/70/20);

acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw
(40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw
(25/65/15);

acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw
(60/25/15);

acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

The silicone-containing copolymers described above can be synthesized by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179 - 318.

In compositions according to the invention it can be desirable to purify the silicone containing copolymer by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as

above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer is solubilized by supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurised and dry, extracted polymer is recovered from the extraction vessel.

The hair styling polymers herein are utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. The present development relates to the neutralisation of a hair fixative polymer (eg silicone grafted tBA/AA copolymer) with a neutralisation system consisting essentially of a specific inorganic base, namely sodium hydroxide, in anhydrous or essentially anhydrous aerosol and non-aerosol hairsprays and other hair cosmetic products. In particular the present development relates to improving the clarity, long term storage stability, hair feel attributes and ease of removal characteristics of hairspray and other hair cosmetic products containing no or very low levels of water, approximately 0 - 1 %, preferably 0 - 0.7% water, by neutralisation of the hair fixative polymer with a neutralisation system comprising at least 80 %, preferably at least 95 % and more preferably at least 99 % by weight of the neutralisation system of sodium hydroxide. While the neutralisation system can be used in excess of the polymer (for example up to 15 % excess on an equivalent basis) so as to result effectively in 100 % neutralisation of the polymer, nevertheless in preferred compositions, a total of from about 25 % to about 95 %, preferably from about 40 % to about 90 %, more preferably from about 55 % to about 85 %, and especially from about 65 % to about 80 % of the acidic monomers of the polymer are neutralised.

The amount in grams of inorganic base (Z) required to neutralise a polymer can be deduced from calculations which take into account the acid value of the polymer (A); amount of polymer (W); mol wt of the

base (B); mol wt of the acidic moiety (M) and the degree of neutralisation required (N).

$$Z(g) = W \times A/100 \times 1/M \times B \times N\%$$

In the following example the amount of NaOH required to neutralise 2.6g of acrylic acid co-polymer (with acid value of 20) to a level of 77% neutralisation is calculated.

$$Z(g) = 2.6 \times 20/100 \times 1/72 \times 40 \times 0.77$$

$$Z = 0.222 \text{ g}$$

Note the acid value can be experimentally determined by titrating a specific amount of the polymer with base or theoretically by considering the original acidic content of the co-polymer i.e. a polymer with 20% of acid monomer has an acid value of 20.

As described earlier herein, use of the herein defined neutralising system for at least partial neutralisation of the silicone grafted copolymer leads to anhydrous or essentially anhydrous liquid hair cosmetic compositions of improved clarity and long term storage stability. Product clarity can be measured using a visible range spectrophotometer. Using this equipment the percent transmittance of the sample at 450 nm is measured by calibration against a reference sample of Ethanol B100 as 100% transmittance. Typical transmittance values for opaque systems neutralised with potassium hydroxide neutraliser can be as low as from 1 to 5%. In contrast, the compositions of the invention typically display percent transmittance values greater than 80% when first made, preferred compositions herein displaying 80% transmittance values after storage for at least four weeks at 45 C.

The liquid hair cosmetic compositions of the present invention also include a carrier. This can comprise any of those conventionally used in resin hairspray formulations inclusive of solvents, propellants and other optional ingredients of liquid hair cosmetics. The carrier is generally present in the liquid hair cosmetic compositions at from about 70% to

about 99.8%, preferably from about 78% to about 99% by weight. More preferably, the carrier is present at from about 80% to about 98% by weight of the total composition.

Organic solvents suitable for use in the carrier of the present compositions include C₁-C₆ alkanols and ethers, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof. Dimethoxymethane is also a highly preferred solvent.

The performance of the liquid hair cosmetic compositions according to the invention can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at up to a level of 25%, preferable from 1% to 20%, more preferably from 1% to 15%. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapour pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the hair cosmetic carrier is evaporating, since this may excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and J. R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982). See especially in the Appendix of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

Plasticizers suitable for use in compositions of the present invention include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄-C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutyrate, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates,

camphor, glycols, amine derivatives, selected short chain alcohols and castor oil.

Particularly preferred plasticizers for use herein include glycol and citrate based plasticizers such as propylene glycol, dipropylene glycol, acetyl tri-n-butyl citrate, triethylcitrate, tri-n-butyl and acetyl tri-2-ethoxyhexyl citrate (as supplied by Pfizer under the trade name Citroflex (RTM) and also glycerin, amino methyl propanol (AMP), diisobutyladipate (DIBA) and isopropanol.

The present compositions can be formulated as hairsprays in aerosol or non-aerosol forms. If an aerosol hairspray is desired, a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hairspray character.

The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Preferably the density of the propellant or mixture thereof is less than 1 so that pure propellant is not emitted from the container. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether e.g. Dimel 152A (RTM) supplied by Du Pont, propane, n-butane, isobutane, used singly or admixed and propane butane e.g. CAP 80 (RTM). Dimel 152A (RTM) and propane butane are preferred.

The amount of the propellant gas is governed by normal factors well known in the aerosol art. For hairsprays the level of propellant is generally from about 10% to about 40%, preferably from about 20% to about 30%, of the total composition. If a propellant such as dimethylether utilizes vapor pressure suppressant (e.g., trichloroethane or dichloromethane) the amount of suppressant is included as part of the propellant.

The hair spray compositions of the present invention can be made using conventional formulation and mixing techniques. Compositions of the

present invention can be made by adding the polymer to ethanol and mixing for several hours until dissolved. Plasticizer and neutralising ingredients are then added and the resulting solution is stirred. Any remaining ingredients such as water, ethanol and perfume can then be added.

Methods of making the hair cosmetic compositions of the present invention are described more specifically in the examples.

Alternatively, pressurised aerosol dispensers can be used where the propellant is separated from contact with the hairspray composition by use of specialised containers such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in US-A-4,077,441, March 7th 1978, Olofsson and US-A-4,850,577, July 25th 1989, TerStege. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASOON AIRSPRAY (RTM) hairsprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

The liquid hair cosmetic compositions of the present invention can also contain a variety of non-essential, optional components such as preservatives, surfactants, block polymers, thickeners and viscosity modifiers, electrolytes, fatty alcohols, pH adjusting agents, spreading agents, perfume oils, perfume solubilizing agents, sequestering agents; emollients; lubricants and penetrants such as various lanolin components; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; sunscreens and volatile and non-volatile silicone fluids. Such conventional optional ingredients are well known to a person skilled in the art, e.g. surfactants such as anionics (e.g., sodium alkyl sulphates, nonionics (amine oxides) ; amphoterics (aliphatic secondary or tertiary amine derivatives) zwitterionics (aliphatic

quaternary ammonium; phosphonium or sulphonium derivatives) and fluorinated surfactants (e.g. Zonyl FSK) (RTM); thickeners and viscosity modifiers such as diethanolamides of long chain fatty acids; block polymers of ethylene oxide and propylene oxide such as Pluronic (RTM) F88 offered by BASF Wyandotte; fatty alcohols such as cetearyl alcohol; viscosity modifiers such as sodium chloride, sodium sulphate, and ethyl alcohol; electrolyte such as earth and alkaline-earth metal salts; quaternary ammonium ions and cationic amines and halogen ions; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; spreading agents such as isododecane, perfume oils such as Florasynth (RTM) perfumes; perfume oil solubilizers such as polyethylene glycol fatty acid esters and sequestering agents such as ethylenediamine tetraacetic acid. Each of these optional materials can be present at a level of from about 0.05% to about 5%, preferably from about 0.1% to about 3% by weight of composition.

The liquid hair cosmetic compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits desired considering the length and texture of the hair.

The invention is illustrated by the following non-limiting examples.

In the examples, all concentrations are on a 100% active basis, unless otherwise stated and the abbreviations have the following designation:

Hair Styling Polymer - 60% t-butyl acrylate/20% acrylic acid/20% silicone PDMS. Weight average molecular weight (measured by SEC) of 150,000.

NaOH - Sodium hydroxide solution, containing 45% sodium hydroxide and 55% water.

Solvent - Ethanol

Examples I-VI

The following are liquid hair cosmetic compositions in the form of hairspray compositions suitable for pump spray dispensers and which are representative of the present invention:

	I	II	III	IV	V	VI
Hair Styling Polymer	3.0	2.0	4.0	6.0	2.0	5.0
% poly NaOH neutralised	82	70	75	80	85	75
Balance	-----to 100 percent with ethanol-----					

The balance contains ethanol and optional ingredients such as plasticizer (preferably DIBA), perfume and surfactants.

The hairspray formulations are prepared by adding the polymer directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. The neutralizing agent is then added and mixed into the premix. Then, the optional ingredients, as may be applicable, are mixed into the composition.

The above compositions provide effective style retention, deliver a hair conditioning effect and have excellent long term clarity and a non-tacky hair feel.

Examples VII-XII

The following are liquid hair cosmetic compositions in the form of hairspray concentrate compositions suitable for aerosol dispensers and which are representative of the present invention:

VII VIII IX X XI XII

Hair Styling Polymer	4.0	2.0	5.0	6.0	3.0	7.0
% poly NaOH neutralised	70	78	85	78	80	75
Balance	----- to 100 percent with solvent -----					

As in examples I to VI the balance is ethanol and optional ingredients such as plasticizer (preferably DIBA), perfume and surfactants. The above compositions are prepared as in Examples I-VI. The concentrates are packaged in conventional aerosol spray cans and are charged with a conventional liquifiable propellant such as CAP 80 (RTM) at a propellant:concentrate weight ratio of 23:77.

The above compositions have excellent clarity and stability characteristics and when applied to the hair, provide good hair styling and conditioning benefits as well as a non-tacky hair feel and improved ease of removal.

WHAT IS CLAIMED IS:

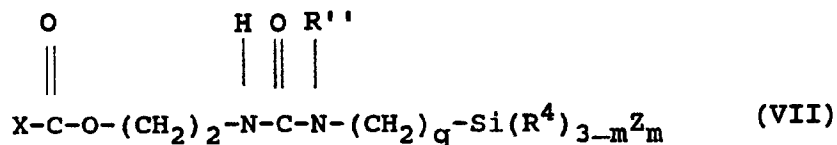
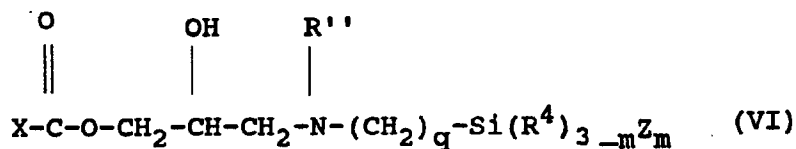
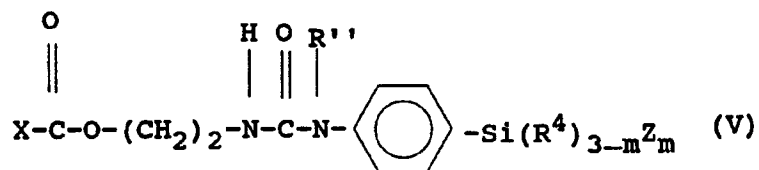
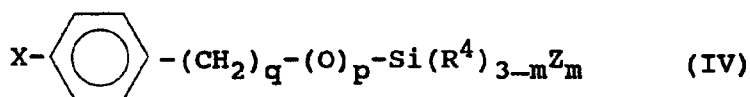
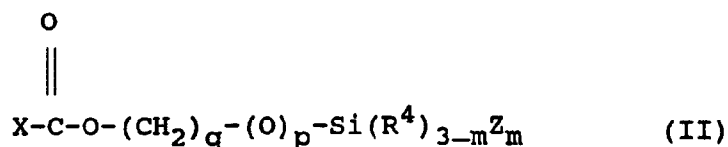
1. A liquid hair cosmetic composition comprising:-
 - (a) from about 0.1% by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25% of the acid groups on the silicone-containing copolymer;
 - (c) from 0% to about 1.0% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.
2. A liquid hair cosmetic composition according to Claim 1 wherein the silicone-containing macromer has the general formula (I):



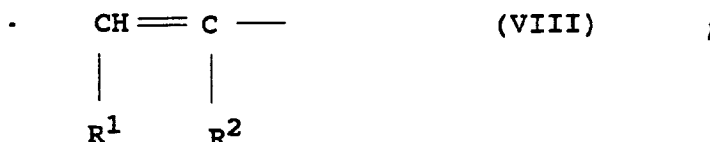
wherein X is a vinyl group; Y is a divalent linking group; R is hydrogen, alkyl, aryl, alkylamino, trialkylsiloxy or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500; n is 0 or 1; and m is an integer from 1 to 3.

3. A liquid hair cosmetic composition according to Claim 1 or 2 wherein the silicone-containing copolymer has a weight average molecular weight of from 10,000 to 1,000,000 comprising a hydrophilic carboxylate containing monomer (B), optionally a lipophilic, low polarity, free-radically polymerizable vinyl

monomer (A) which is copolymerizable with B, and a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, based on polydimethylsiloxane and wherein the macromer (C) is selected from one or more monomers having the general formulae (II - VII):



wherein m is 1, 2 or 3; p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; X is



R^1 is hydrogen or $-\text{COOH}$; R^2 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$; Z is



R^4 is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 1% to 98% monomer B, and from 0.1% to 50% monomer C.

4. A liquid hair cosmetic composition according to any of Claims 1 to 3 wherein the silicone-containing copolymer comprises from 5% to 92% by weight monomer A, from 7.5% to 80% by weight monomer B, and from 0.1% to 50% monomer C.
5. A liquid hair cosmetic composition according to any of Claims 1 to 4 wherein monomer A is selected from acrylic acid esters of C_1 - C_{18} alcohols, methacrylic acid esters of C_1 - C_{18} alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.
6. A liquid hair cosmetic composition according to any of Claims 1 to 5 wherein monomer B is selected from acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid and mixtures thereof; and is preferably selected from acrylic acid and methacrylic acid and mixtures thereof.

7. A liquid hair cosmetic composition according to any of Claims 3 to 6 wherein the silicone containing macromer has the general formula (II) in which $p = 0$ and $q = 3$, m is 1, R^4 is alkyl, R^1 is hydrogen and R^2 is methyl.
8. A liquid hair cosmetic composition according to any of Claims 1 to 7 wherein the silicone-containing copolymer is selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 molecular weight (mw) (10/70/20);
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (20/60/20 w/w/w)
acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)
t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw (60/20/20)
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);
acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);
acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/15);
acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw (60/25/15);
acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.
9. A liquid hair cosmetic composition according to any of Claims 1 to 8 wherein the silicone-containing copolymer is neutralised to a level of from about 40% to about 90%, preferably from about 55% to about 85%, more preferably from about 65% to about 80% with sodium hydroxide.
10. A liquid hair cosmetic composition according to any of Claims 1 to 9 containing less than 0.7% by weight water.

11. A liquid hair cosmetic product comprising a hairspray composition and spray dispenser means for containing and spraying the hairspray composition, and wherein the hairspray composition comprises:
- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25% of the acid groups on the silicone-containing copolymer;
 - (c) from 0% to about 1.0% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04756

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61K 7/11

US CL :424/70.12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70.12, 70.121, 70.122, DIG1, DIG2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,192,861 (MICCHELLI) 11 March 1980, see abstract, column 2 lines 8-21, column 3 lines 41-62.	1-3, 11
A	US, A, 4,693,935 (MAZUREK) 15 September 1987, see claims 1-13.	1-3, 11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be part of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E earlier document published on or after the international filing date	*Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A document member of the same patent family
*O document referring to an oral disclosure, use, exhibition or other means	
*P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 JUNE 1995

Date of mailing of the international search report

21 JUL 1995

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04756

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

